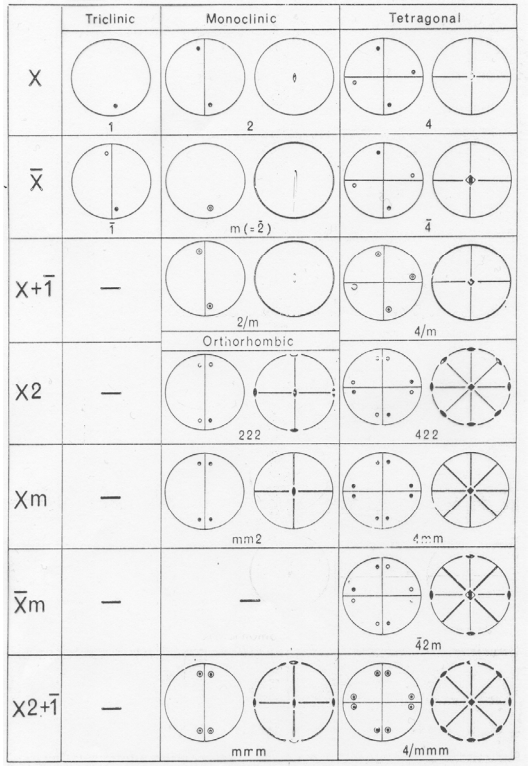
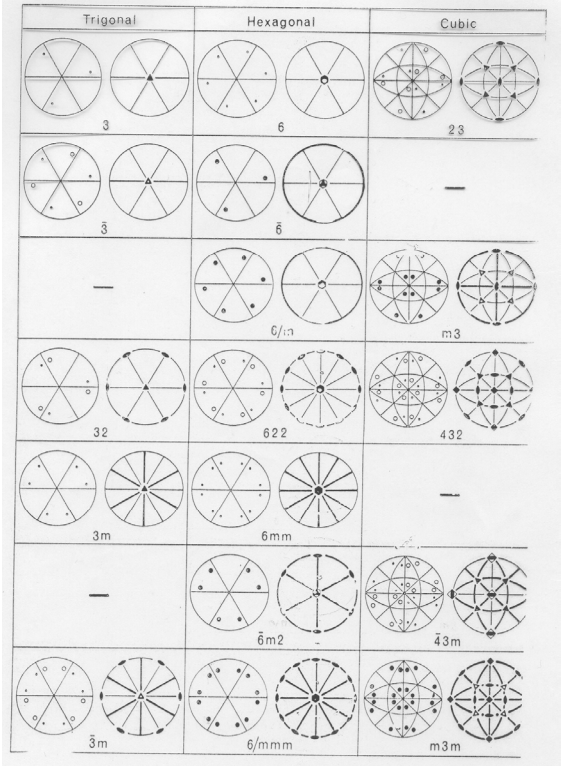




There are 230 space-groups!

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.

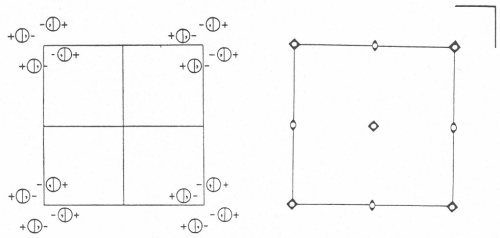
n_m -> n for a screwaxis
a,b,c,d or n -> m for glide plane

Example:

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

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

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



Origin at centre (4/*m*)

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

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
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) $\bar{y},x,\bar{z}$	General: no conditions
4	*k*	*m* . .	$x,y,\frac{1}{4}$	$\bar{x},\bar{y},\frac{1}{4}$	$\bar{y},x,\frac{1}{4}$	$y,\bar{x},\frac{1}{4}$	Special:
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 . .	$0,\frac{1}{2},z$	$\frac{1}{2},0,z$	$0,\frac{1}{2},\bar{z}$	$\frac{1}{2},0,\bar{z}$	no extra conditions
2	*h*	4 . .	$\frac{1}{2},\frac{1}{2},z$	$\frac{1}{2},\frac{1}{2},\bar{z}$			$hkl: h+k=2n$
2	*g*	4 . .	$0,0,z$	$0,0,\bar{z}$			no extra conditions
2	*f*	2/*m* . .	$0,\frac{1}{2},\frac{1}{4}$	$\frac{1}{2},0,\frac{1}{4}$			no extra conditions
2	*e*	2/*m* . .	$0,\frac{1}{2},0$	$\frac{1}{2},0,0$			$hkl: h+k=2n$
1	*d*	4/*m* . .	$\frac{1}{2},\frac{1}{2},\frac{1}{4}$				$hkl: h+k=2n$
1	*c*	4/*m* . .	$\frac{1}{2},\frac{1}{2},0$				no extra conditions
1	*b*	4/*m* . .	$0,0,\frac{1}{4}$				no extra conditions
1	*a*	4/*m* . .	$0,0,0$				no extra conditions
							no extra conditions

Symmetry of special projections

Along [001] *p* 4 — $a'=a$ $b'=b$ — Origin at $0,0,z$

Along [100] *p* 2*m m* — $a'=b$ $b'=c$ — Origin at $x,0,0$

Along [110] *p* 2*m m* — $a'=\frac{1}{2}(-a+b)$ $b'=c$ — 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]$P\,4_2/m\,(c'=2c)$; [2]$C\,4/a\,(a'=2a, b'=2b)(P\,4/n)$; [2]$F\,4/m\,(a'=2a, b'=2b, c'=2c)(I\,4/m)$

Maximal isomorphic subgroups of lowest index

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

Minimal non-isomorphic supergroups

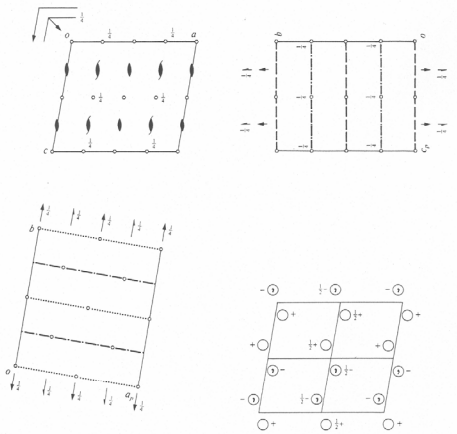
I [2]$P\,4/m\,m\,m$; [2]$P\,4/m\,c\,c$; [2]$P\,4/m\,b\,m$; [2]$P\,4/m\,n\,c$

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

$C\,2/c$ C_{2h}^6 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 $0\le x\le\frac{1}{4}$; $0\le y\le\frac{1}{4}$; $0\le z\le\frac{1}{4}$

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

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		Reflection conditions
	(0,0,0)+	(½,½,0)+	
8 f 1	(1) x,y,z	(2) $\bar{x},y,z+\frac{1}{2}$ (3) $\bar{x},\bar{y},\bar{z}$ (4) $x,\bar{y},z+\frac{1}{2}$	General: $hkl: h+k=2n$ $h0l: h,l=2n$ $0kl: k=2n$ $hk0: h+k=2n$ $0k0: k=2n$ $h00: h=2n$ $00l: l=2n$
4 e 2	0,y,¼	0,ȳ,¼	Special: as above, plus no extra conditions
4 d $\bar{1}$	¼,¼,½	¼,¼,0	$hkl: k+l=2n$
4 c $\bar{1}$	½,½,0	½,½,½	$hkl: k+l=2n$
4 b $\bar{1}$	0,½,0	0,½,½	$hkl: l=2n$
4 a $\bar{1}$	0,0,0	0,0,½	$hkl: l=2n$

O

Cu

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] $C1211$ $(C2)$ (1; 2)+
[2] $C1\bar{1}1$ $(P\bar{1})$ (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)+(½,½,0)
[2] $P12_1/n1$ $(P2_1/c)$ 1; 3; (2; 4)+(½,½,0)
[2] $P12_1/c1$ $(P2_1/c)$ 1; 4; (2; 3)+(½,½,0)

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] $Immm a$; [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

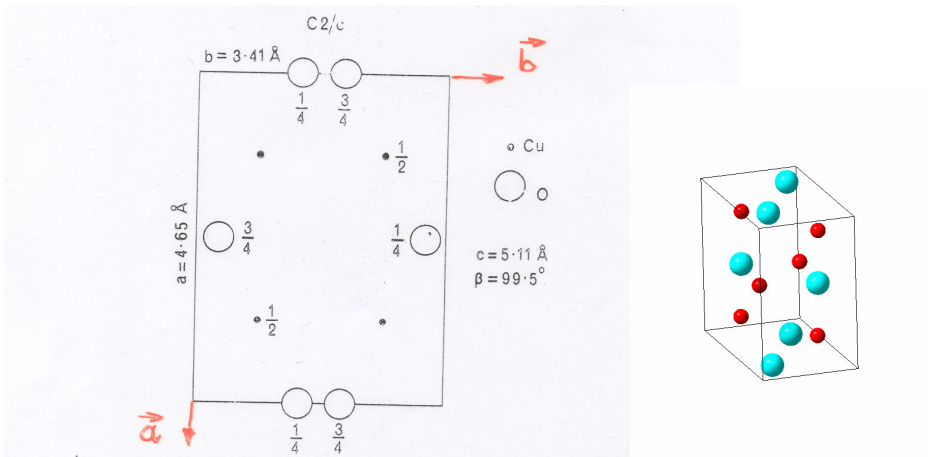
Corresponding crystallographic point group: 2/m

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)

Tema:

- Rekapituler kjemisk binding. Når kan atomer/enheter beskrives ved kuler. Når har en typiske retningsavhengige bindinger.
- Ideell kulepakking.
  Avvik forventes når….
  Ionestruktur og kulepakking
- 1D og 2D tetteste kulepakking
- Fordypninger i lag
  A,B,C posisjoner (i projeksjonsplan)
- Stablemåter tetteste
- Hcp, ccp + polytyper
- Demonstrere tilstedeværelse av hulrom mellom to tetteste pakkede lag. Angi koordinasjonstall + polyedergeometri.

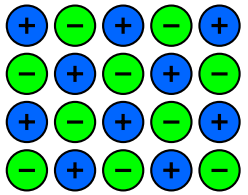
Table 1.2 *Types of solids*

Type	Units present	Characteristics	Examples	Approximate cohesive energy, 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 CH_4	7.6 10
Hydrogen-bonded	Molecules held together by hydrogen bonds	Low melting insulators	H_2O (ice) HF	50 30

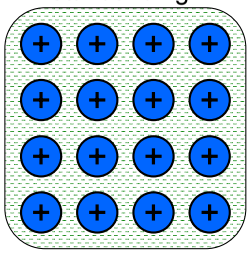
Atoms as spheres:

- ions
- metal atoms
- molecules

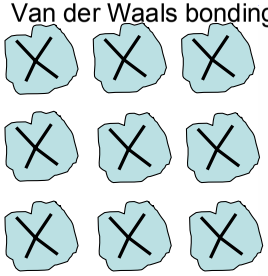
Ionic bonding

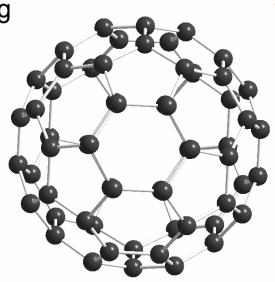


Metal bonding

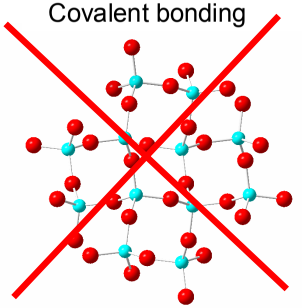


Van der Waals bonding





Covalent bonding



Spherepacking

The entities have to be:

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

Ideal sphere packing model

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

Closest (densest) packing of spheres:

74% of the volume is filled by the spheres

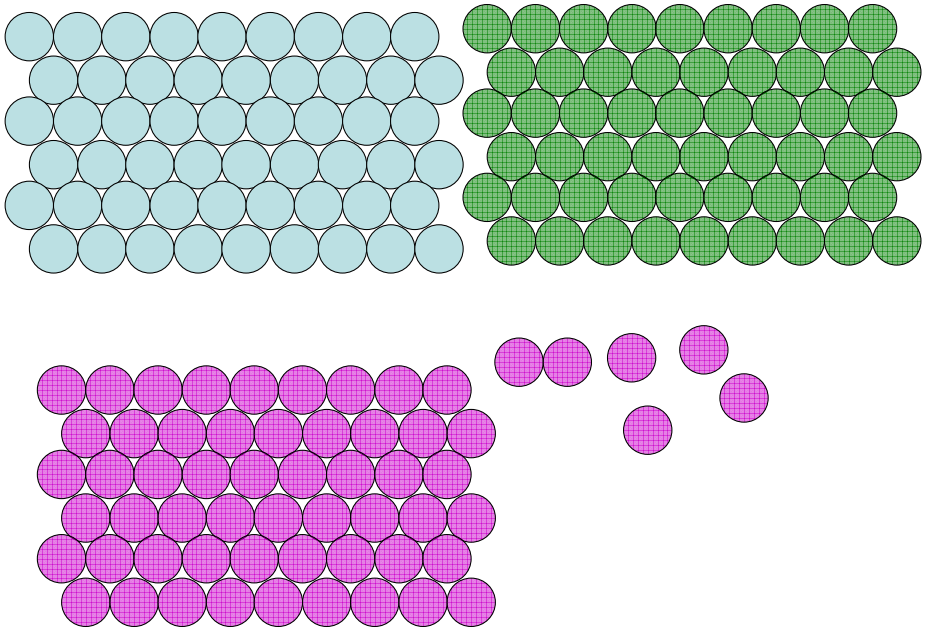
26% voids / vacant space

The voids/holes will have different appearance:

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

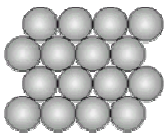
The voids/holes may be filled with atoms

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

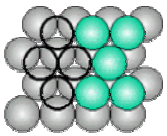


AB……	hcp	hexagonal close packed
ABC…..	ccp	cubic close packed
AA…..		primitive hexagonal packing

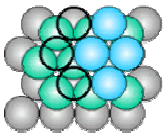
Dense sphere packing



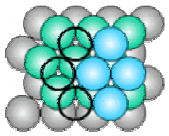
A



AB



ABA

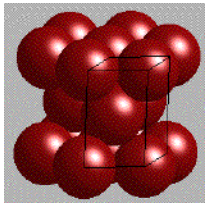


ABC

hcp

ccp

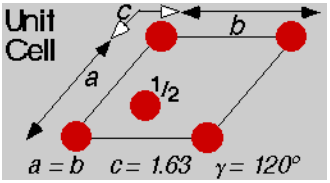
hcp (hexagonal close packed)

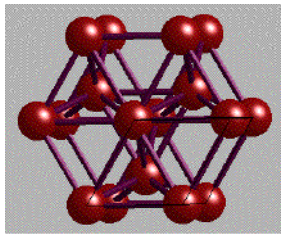


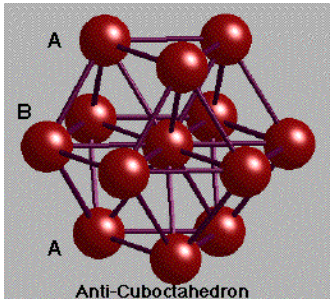
Z = 2

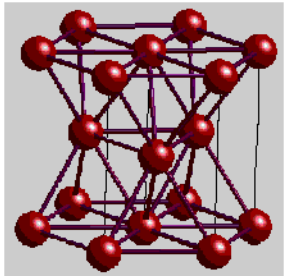
2 atoms in unitcell:

(0, 0, 0), ($^{2}/_{3}$, $^{1}/_{3}$, $^{1}/_{2}$)

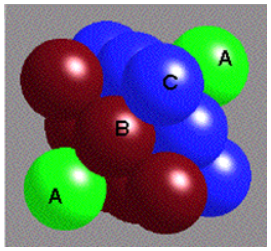








ccp (cubic close packed)

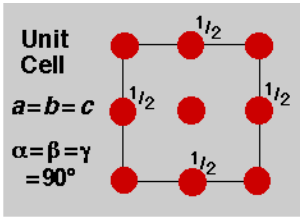


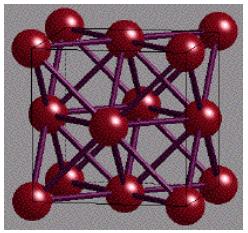
Z=4

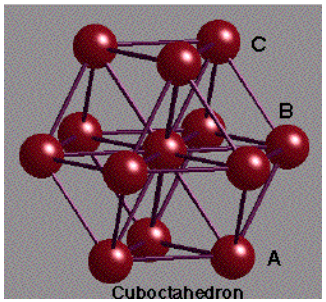
4 atoms in unitcell:

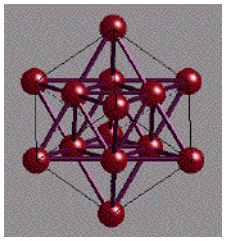
(0, 0, 0) (0, $^1/_2$, $^1/_2$)

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

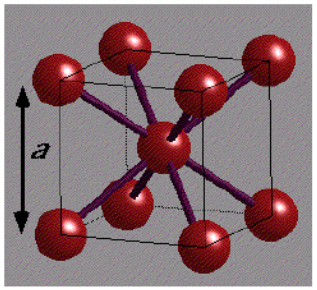






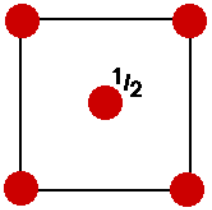


bcc



Body-Centred Cubic

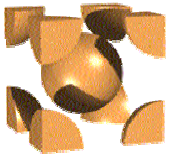
BCC

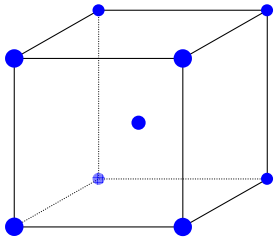


Z=2

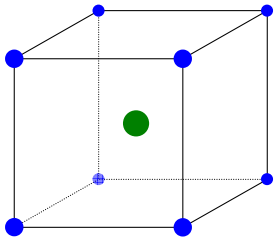
2 atoms in unitcell:

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

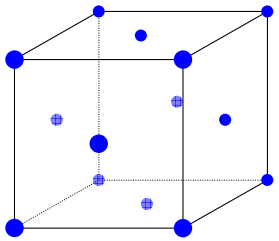


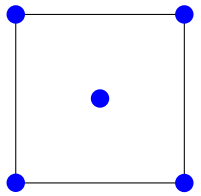


bcc, cucic, I-centered
(0,0,0) + (1/2,1/2,1/2)
CN = 8



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

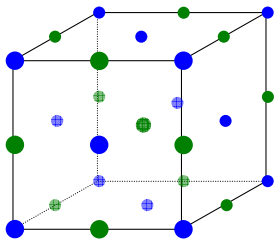


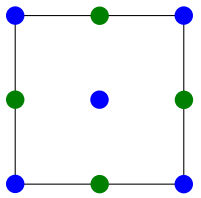


fcc, Cubic F-centered lattice

Structure = lattice + basis (motif)

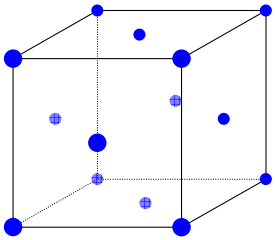
F-centered lattice with metal in (0,0,0)

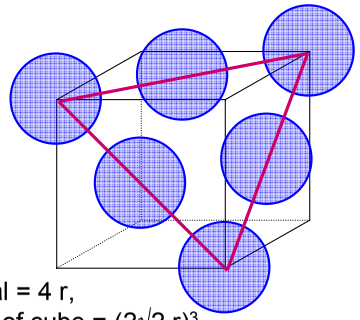




NaCl-type structure = cubic + basis

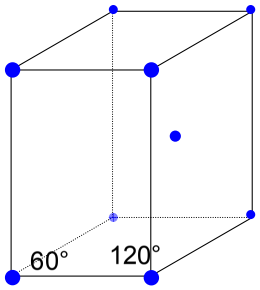
F-centered lattice:
Na in (0,0,0)
Cl in (1/2,0,0)

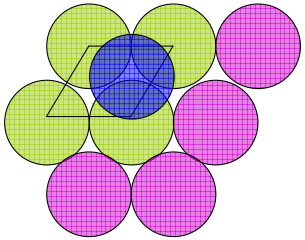




(111)

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

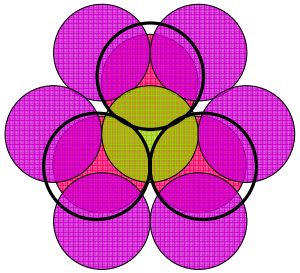




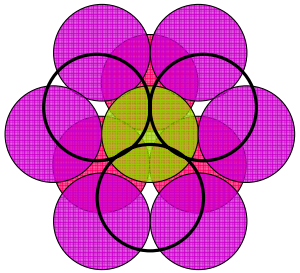
Density of packing

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

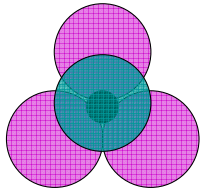
hcp



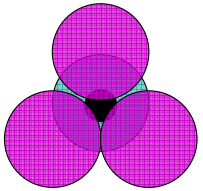
fcc



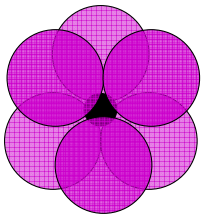
Tetraeder hole +

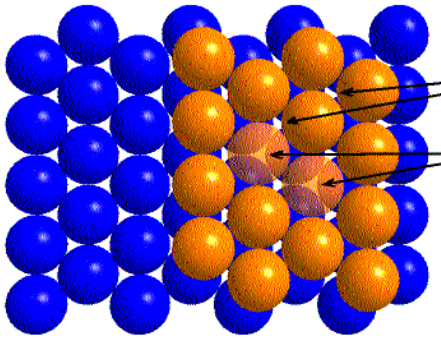


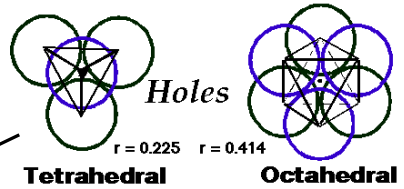
Tetraeder hole -

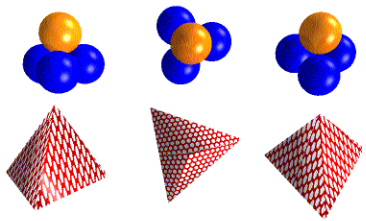


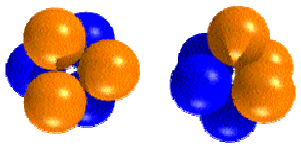
Octaeder hole





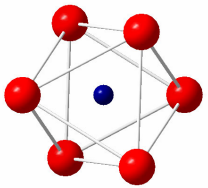






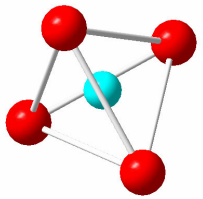
Octahedra holes

CN = 6



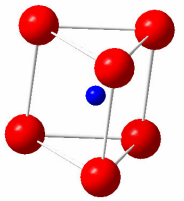
Tetrahedra holes

CN = 4



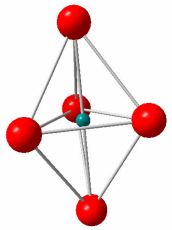
Hexagonal packing (AA..)
Trigonal prismatic holes

CN = 6

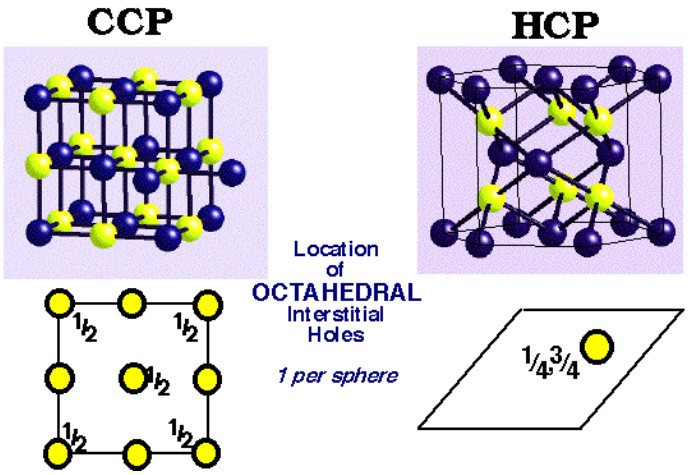


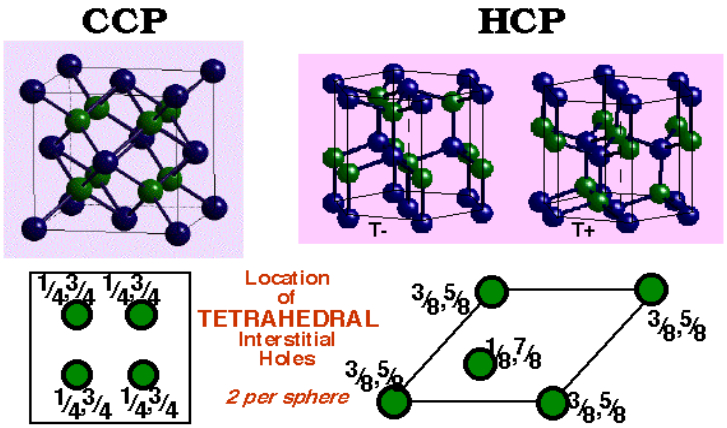
Hexagonal closepacked (AB..)
Trigonal bipyramidal

CN = 5



Type of hole	*Number*	*Max. radius*
Trigonal prismatic	2N	0.528
Tetragonal	2N	0.225
Octahedral	N	0.414





Crystal plane and crystal directions

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

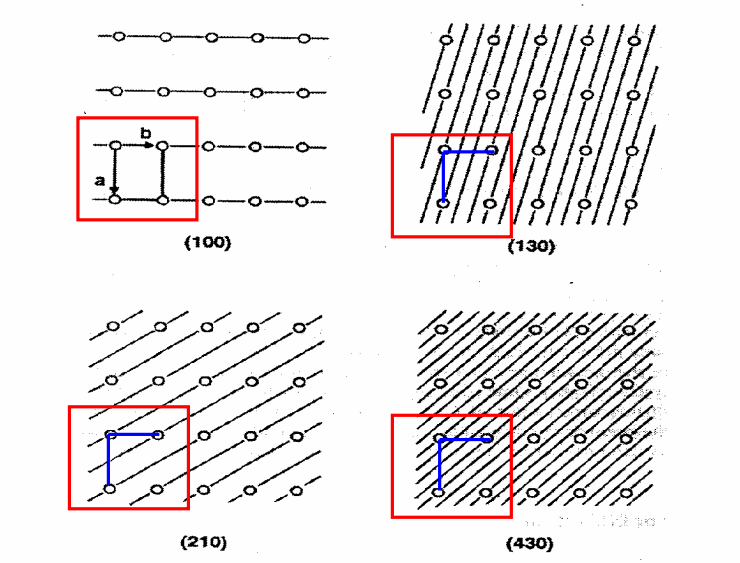
The equivalent planes and directions are a result of the systems symmetry

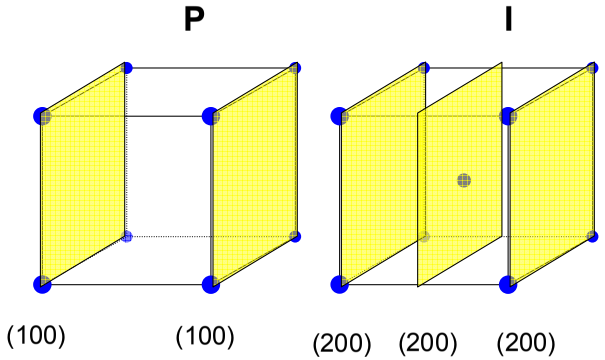
e.g. fcc <111>

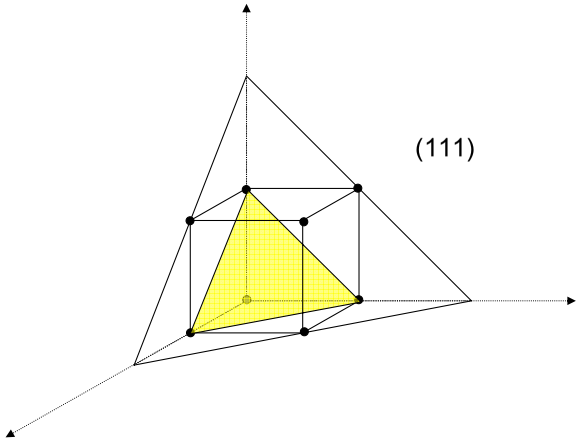
[111] [$\bar{1}$11] [$\bar{1}\bar{1}$1] [1$\bar{1}$1]

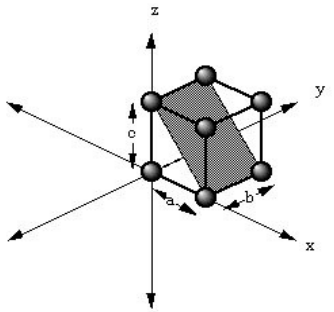
[$\bar{1}\bar{1}\bar{1}$] [1$\bar{1}\bar{1}$] [11$\bar{1}$] [$\bar{1}$1$\bar{1}$]

Miller indices, 2D

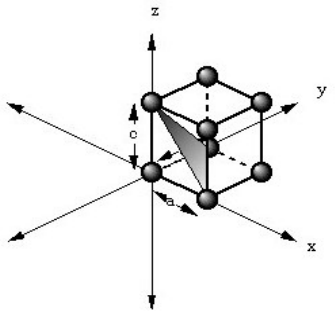




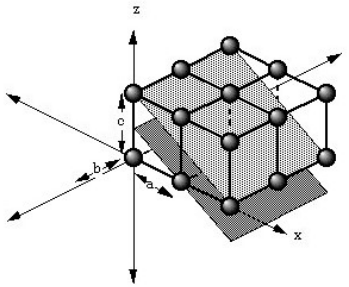




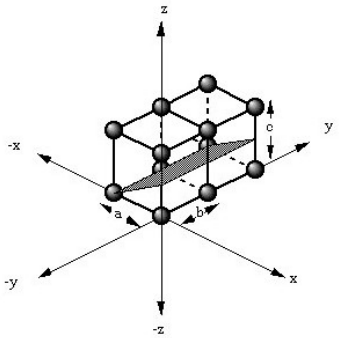
	a	b	c
intercept length	1	∞	1
reciprocal	$\frac{1}{1}$	$\frac{1}{\infty}$	$\frac{1}{1}$
cleared fraction	1	0	1
Miller indice	(101)		



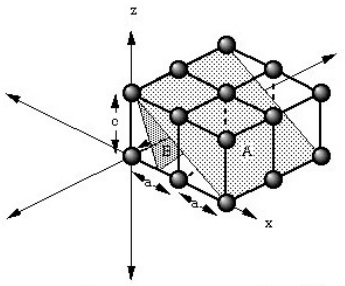
	a	b	c
intercept length	1	1	1
reciprocal	$\frac{1}{1}$	$\frac{1}{1}$	$\frac{1}{1}$
cleared fraction	1	1	1
Miller indice	(111)		



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

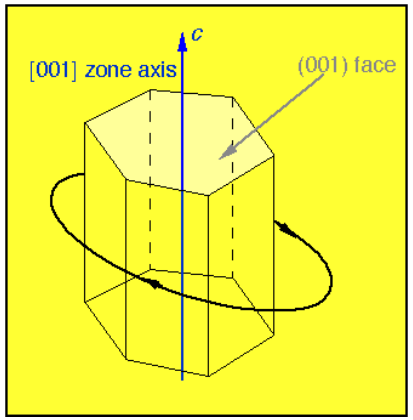


	a	b	c
intercept length	-1	∞	$\frac{1}{2}$
reciprocal	$\frac{1}{-1}$	$\frac{1}{\infty}$	$\frac{1}{1/2}$
cleared fraction	-1	0	2
Miller indice	($\bar{1}$02)		

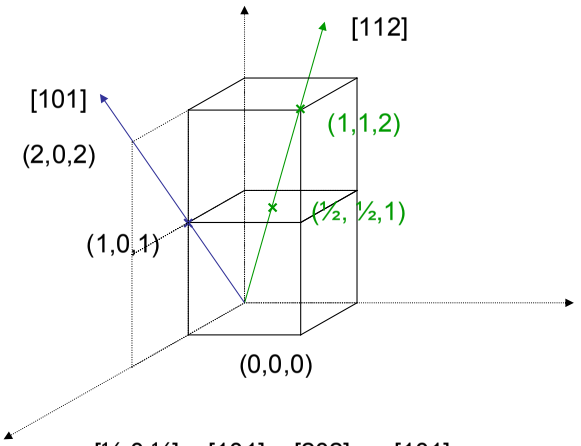


plane A plane B

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

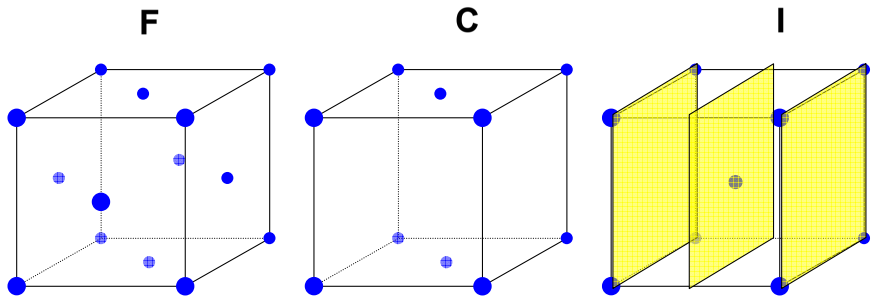


Directions



[½ 0 ½] = [101] = [202] = n[101]

Parallel directions have same index



Conditions for bragg reflexes.

hkl; h+k = 2n
all odd
all even

h+k = 2n

h+k+l = 2n

P lattice has no conditions

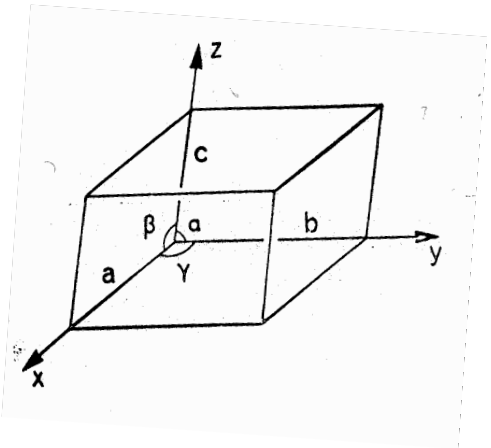
In addition to this, there will be effects from: screw axis and glide planes.

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

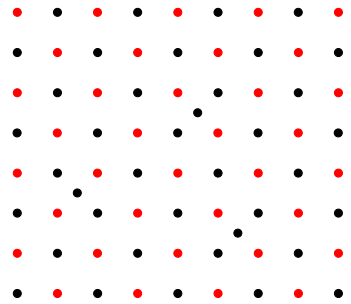
ρ_{obs}

ρ_{calc}

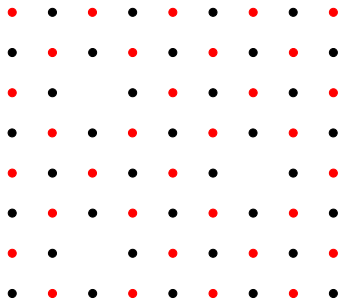
- V unitcell; is determined experimentally
- Formula weight

↓

Model assumptions:
A/B < 1

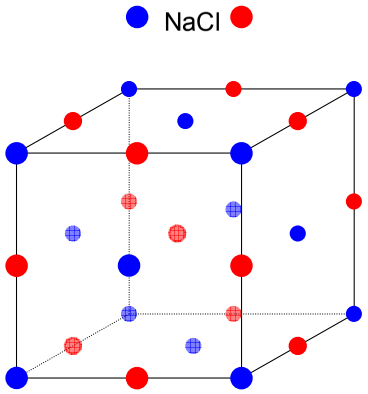


AB_{1+y}

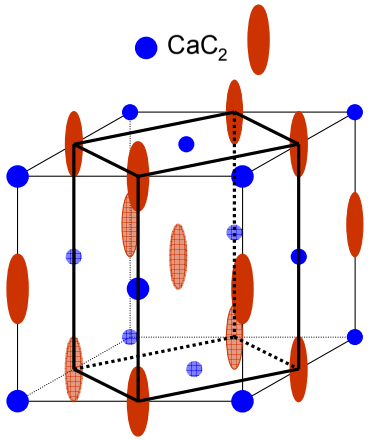


$A_{1-x}B$

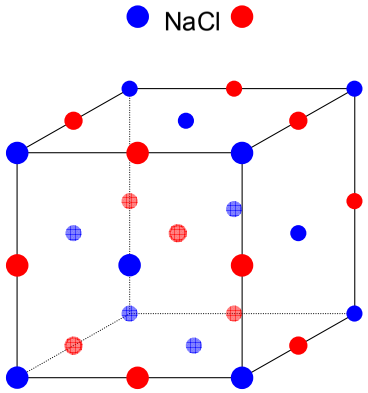
ρ(interstitial B) > ρ(perfect) > ρ(vacant space A)



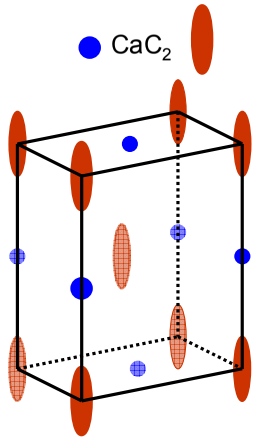
Cubic
z = 4



Non-cubic



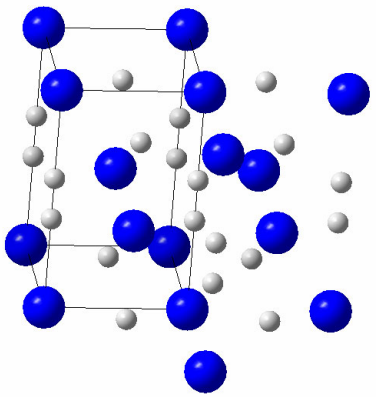
Cubic
z = 4



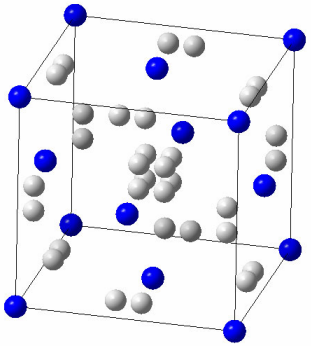
Non-cubic

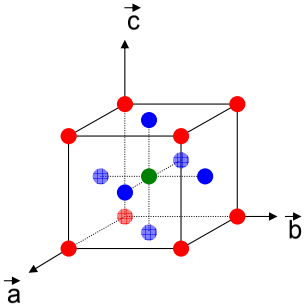
Tetragonal
z = 2

CaC_2 (lt)



CaC_2 (ht)

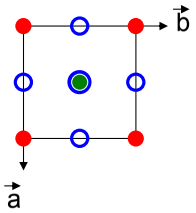




ABO_3

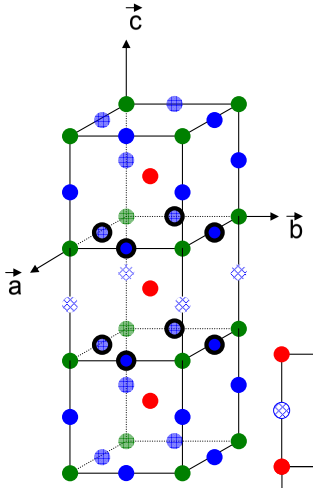
Perovskite
a=b=c, α=β=γ=90°
cubic

Projection on the ab-plane:



ac-plane
bc-plane
} Identical

Cell dimensions are determined by:
A-O-A

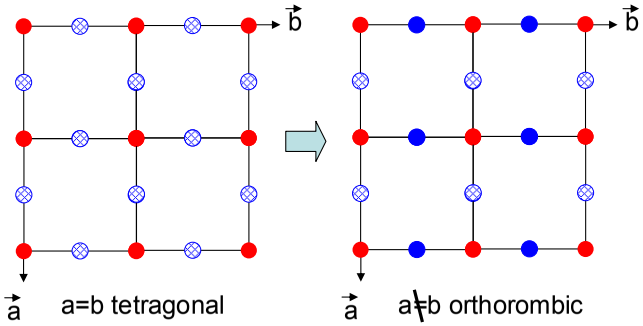


$A_3B_3O_6$ $YBa_2Cu_3O_6$

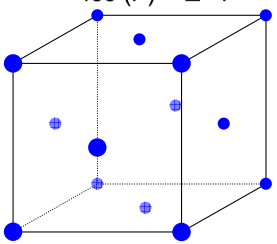
Perovskite
a=b≠c, α=β=γ=90°
Tetragonal

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

Projection on the ab-plane:

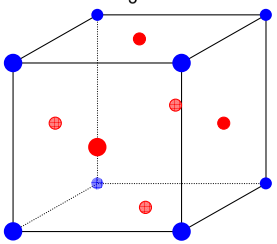


fcc (F) Z=4

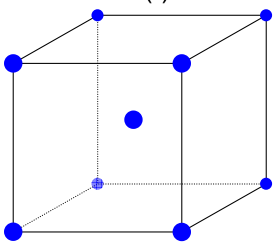


Disordered $Cu_{0.75}Au_{0.25}$
High temp

Low temp
Ordered Cu_3Au



bcc (I) Z=2



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

Low temp
Ordered CuAu