# VIVEKANAD COLLEGE, KOLHAPUR (AUTONOMOUS)

## SOLID STATE PHYSICS

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Date:21/12/2018

# outlines

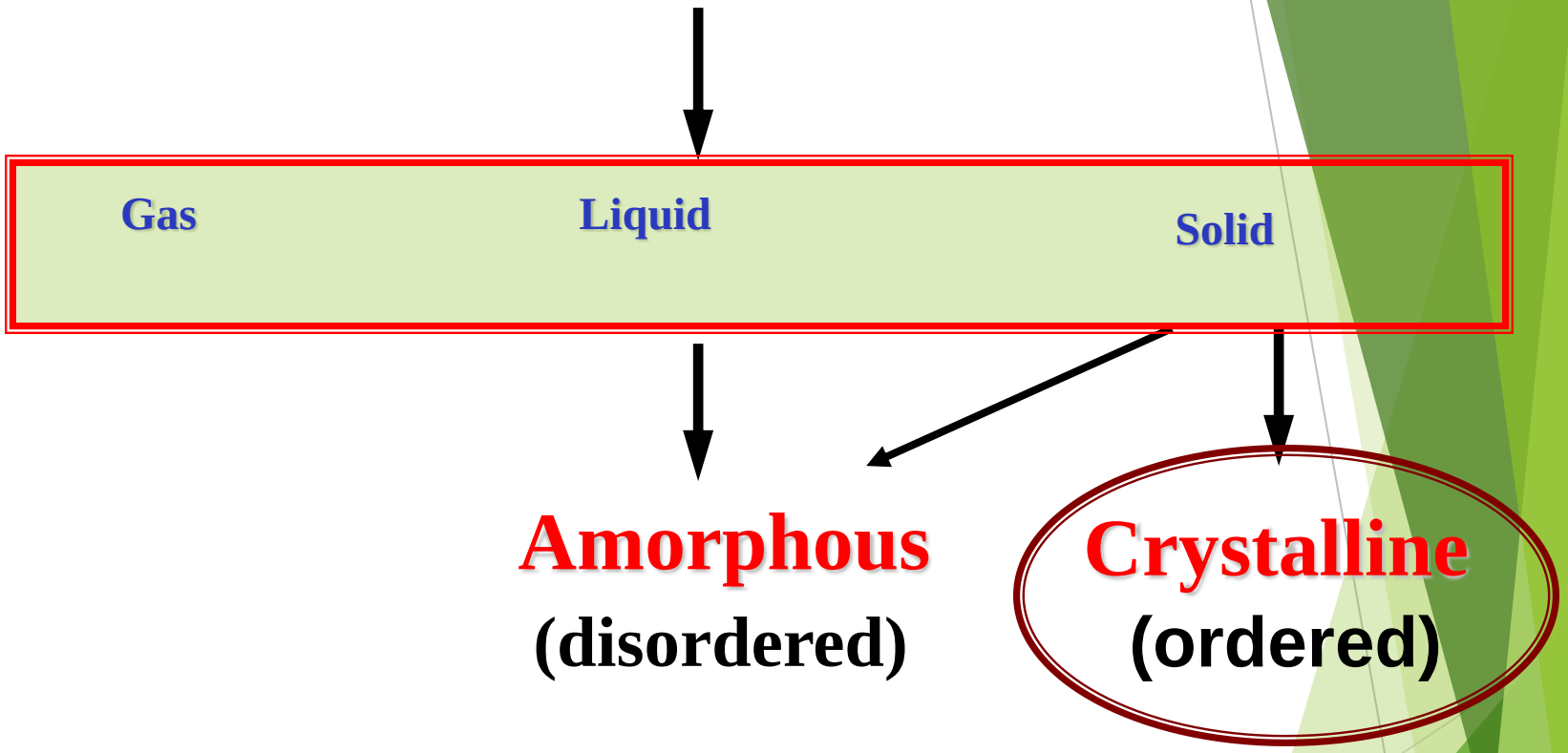
*Introduction*

*Crystalline materials*

*Symmetry*

*Structure of solids*

# States of Matter

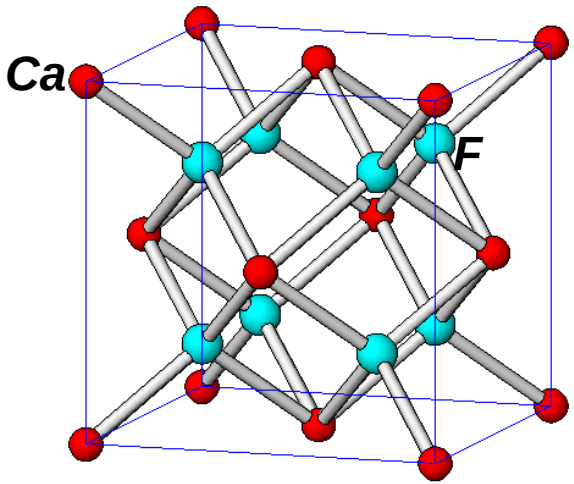


Rogerley Mine, Weardale, England

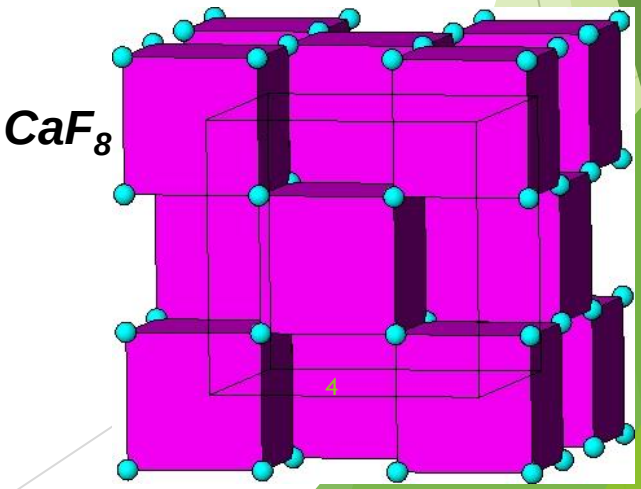
Mina Navidad, Rodeo, Durango, Mexico

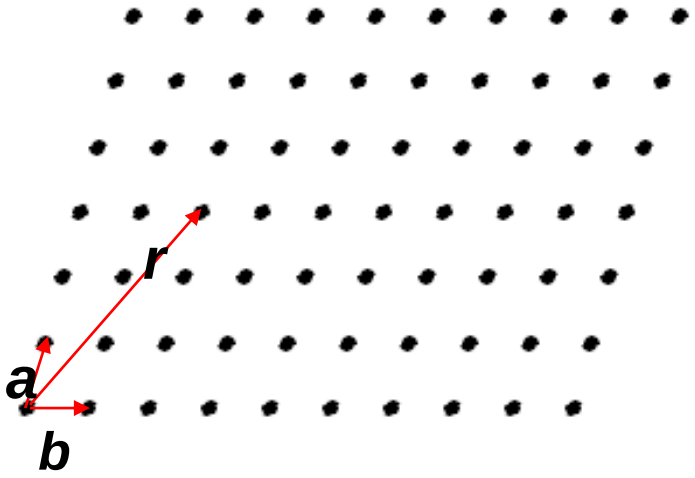
Mont Blanc Massif, Haute-Savoie, France

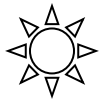
**A crystal is a repeating array of smallest block (unit cell) having a definitely arranged elements.**

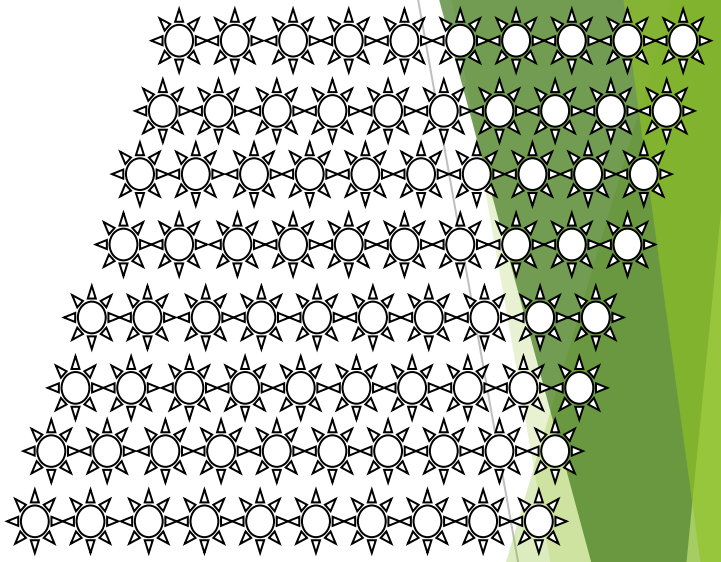



***Fluorite***





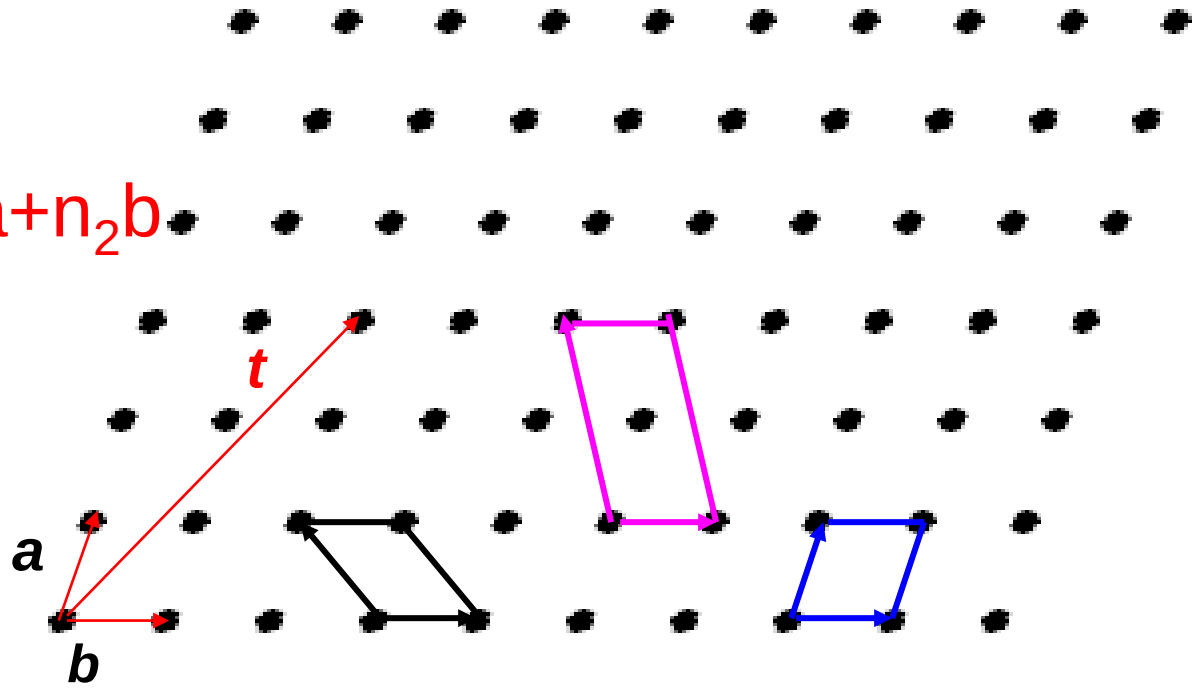


Lattice + Basis (motif) → Crystal structure

**(Real chemical entity)**

# Unit cell

$t = n_1 a + n_2 b$



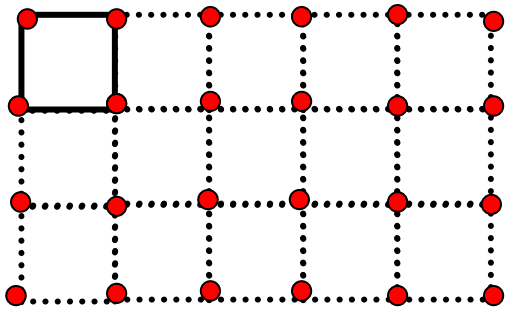

**Unit cell is the smallest repeating part of lattice**
**Have full symmetry of lattice**

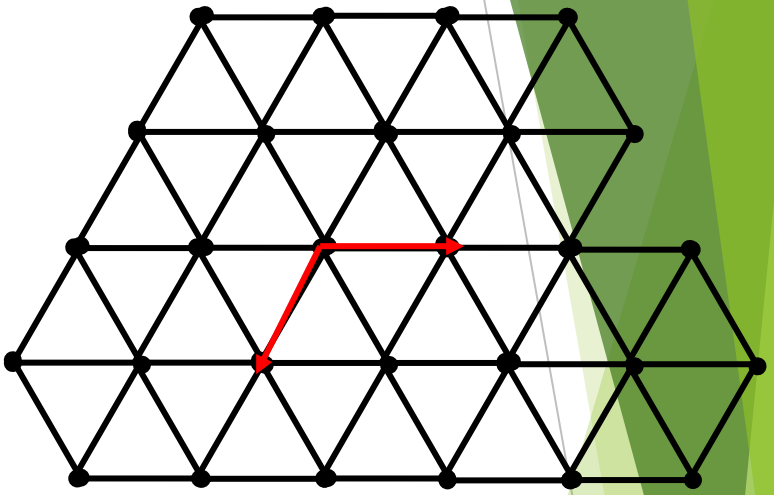
***Primitive or Non-primitive***

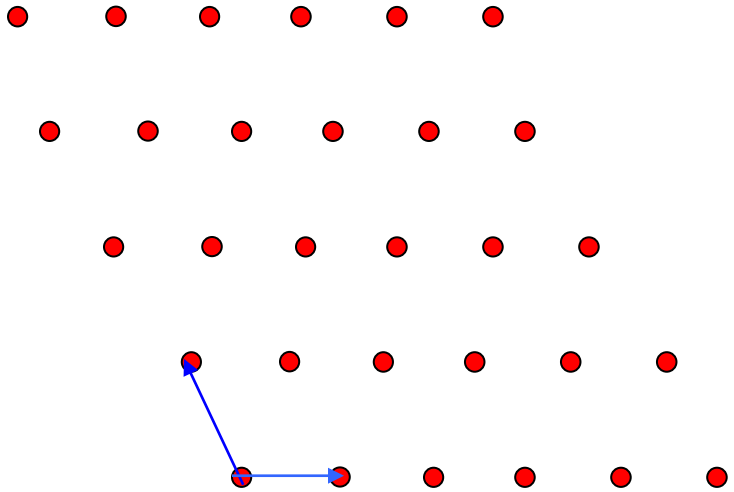
# *Two-dimensional lattice*

**4 crystal systems**

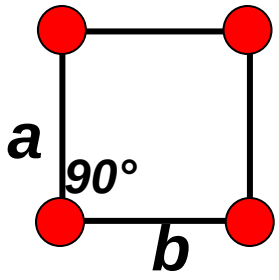
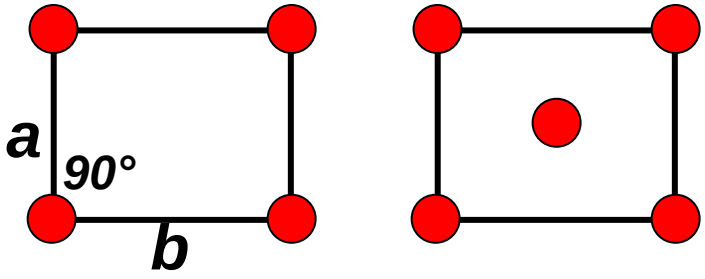
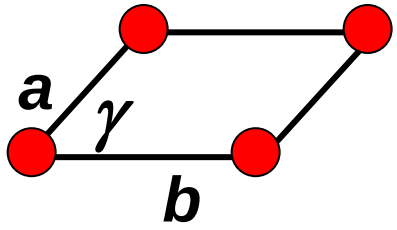
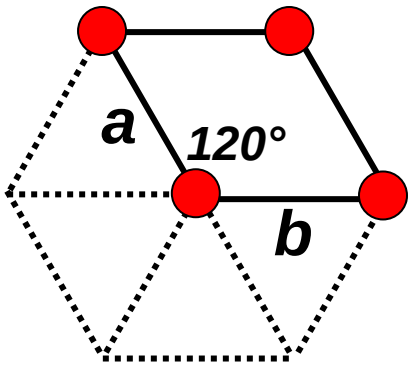
- **oblique**
- **rectangular**
- **square**
- **hexagonal**



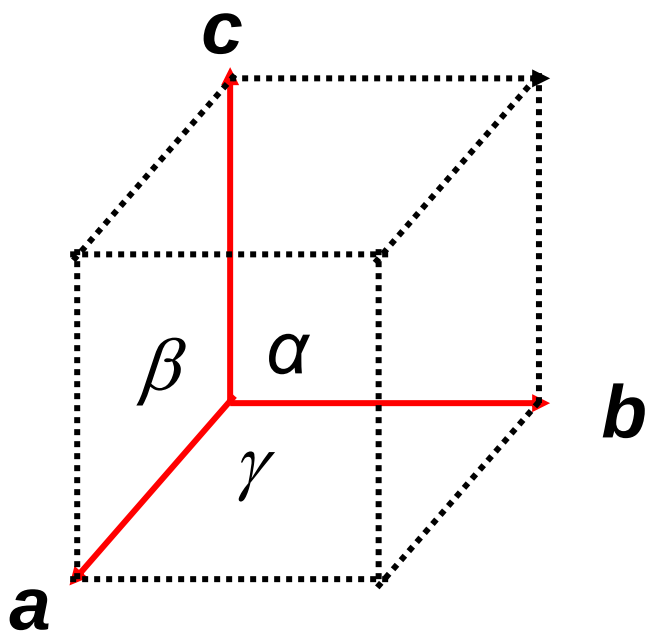




# Crystal system

| | | Bravais lattice | Sym. |
|---|---|---|---|
| $a = b$<br>$\gamma = 90°$ |  | P | One 4 |
| $a \neq b$<br>$\gamma = 90°$ |  | P, C | Two 2 |
| $a \neq b$<br>$\gamma \neq 90°$ |  | P | No |
| $a = b$<br>$\gamma = 120°$ |  | P | One 6 |

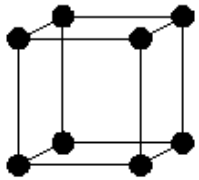
# Convention of unit cell parameters



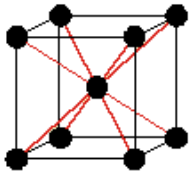
# 3-D crystal System

| | |
|---|---|
| **Cubic** | $a = b = c,\ \alpha = \beta = \gamma = 90°$ |
| **Tetragonal** | $a = b \neq c,\ \alpha = \beta = \gamma = 90°$ |
| **Orthorhombic** | $a \neq b \neq c,\ \alpha = \beta = \gamma = 90°$ |
| **Trigonal** | $a = b = c,\ \alpha = \beta = \gamma \neq 90°$ |
| **Hexagonal** | $a = b \neq c,\ \alpha = \beta = 90°,\ \gamma = 120°$ |
| **Monoclinic** | $a \neq b \neq c,\ \alpha = \beta = 90°,\ \gamma \neq 90°$ |
| **Triclinic** | $a \neq b \neq c,\ \alpha \neq \beta \neq \gamma \neq 90°$ |

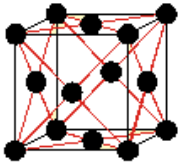
# 7 Crystal systems and 14 Bravais lattices



P

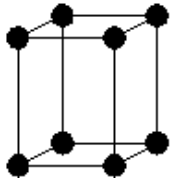


I

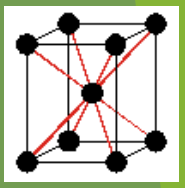


F

Cubic

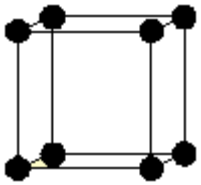


P



I

Tetragonal



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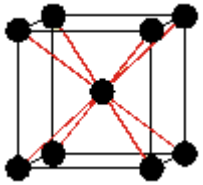
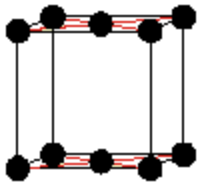
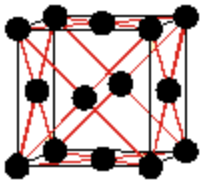


I

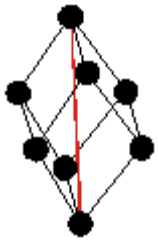


C



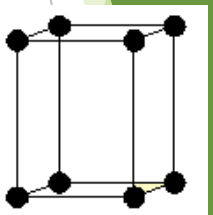
F

orthorhombic



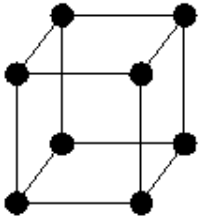
R

Rhombohedral

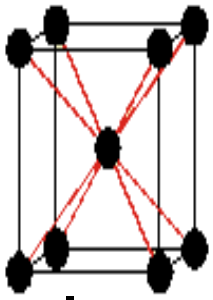


P

Hexagonal

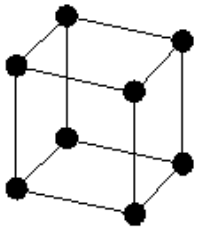


P



I

Monoclinic



P

Triclinic

## *Non-primitive cell*

Number of lattice can be more than one in non-primitive unit cell.

**e.g. F, I, C centered lattices**

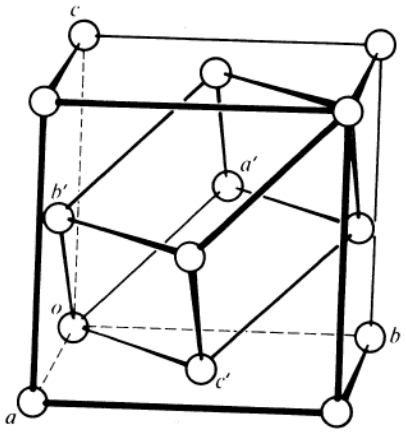
## *Primitive cell*

For any lattice it is possible to find a unit cell where the no lattice points is one.

Primitive cell can also fill the lattice.

Primitive do not have the fill symmetry of lattice.

F



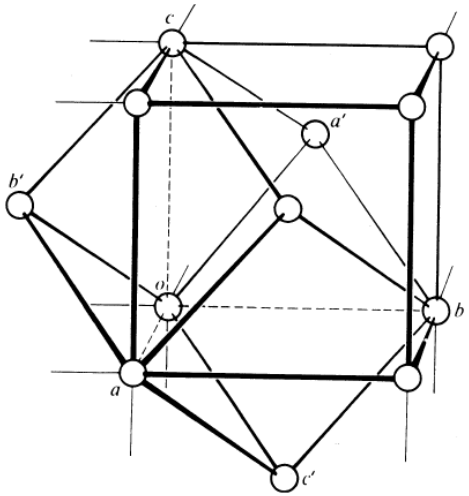

(a+b)/2

(b+c)/2

(c+a)/2

R

I



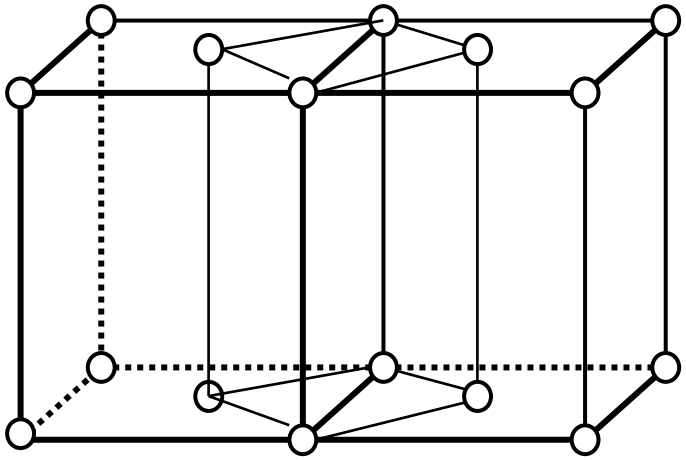

(a+b-c)/2

(b+c-a)/2

(c+a-b)/2

R

C



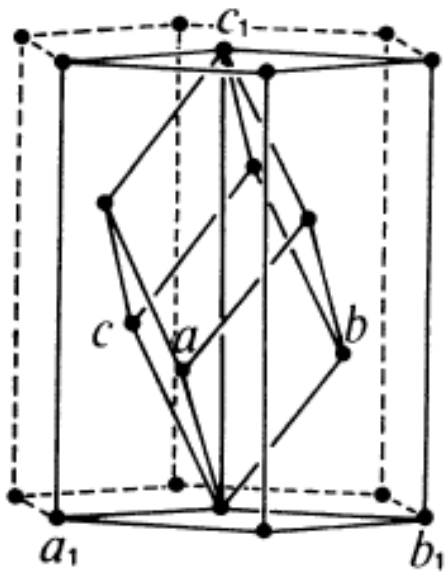
(a-b)/2

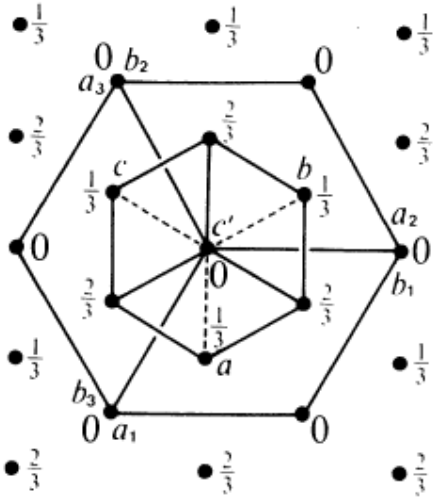
(a+b)/2

c

M

# Haxagonal and rhombohedral system



$$a_r = \frac{2}{3}a_h + \frac{1}{3}b_h + \frac{1}{3}c_h$$

$$b_r = -\frac{1}{3}a_h + \frac{1}{3}b_h + \frac{1}{3}c_h$$

$$c_r = -\frac{1}{3}a_h - \frac{2}{3}b_h + \frac{1}{3}c_h$$

$$a_r{}^2 = a_r \cdot a_r = \frac{1}{3}\sqrt{3a_h^2 + c_h^2}$$

$$a_r \cdot b_r = a_r^2 \cos\alpha$$

$$\cos\alpha = \frac{\frac{1}{3}R^2 - \frac{1}{2}}{\frac{1}{3}R^2 + 1} \qquad R = \frac{c_h}{a_h}$$

# Symmetry

Number of *indistinguishable* configurations a system poses.

**symmetry operation** – an operation performed on an object which leaves it in a configuration that is indistinguishable from, and superimposable on the original configuration.

**symmetry elements** – the points, lines, or planes to which a symmetry operation is carried out.

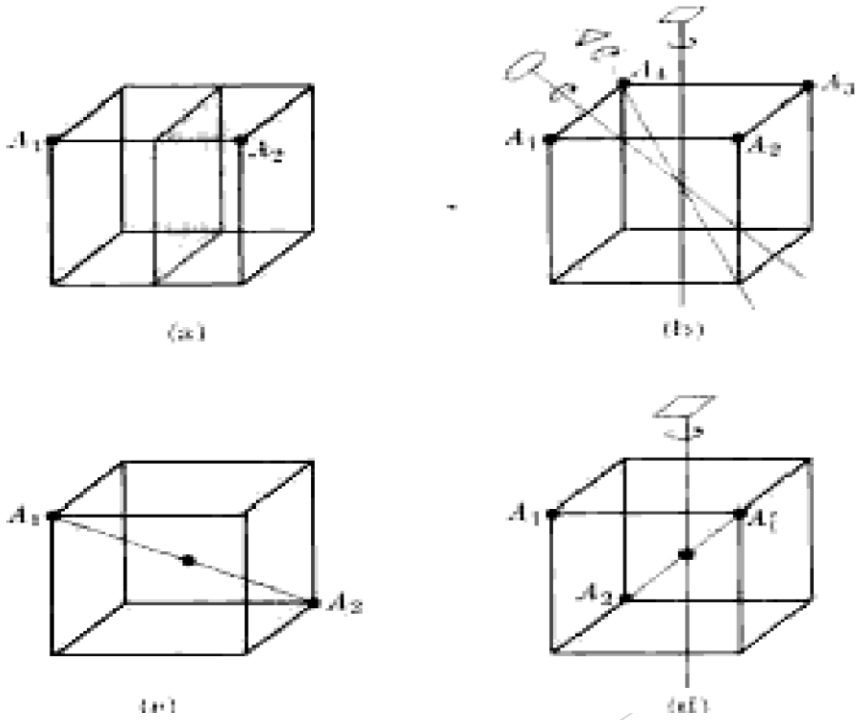
| Element | Operation | Symbol |
|---|---|---|
| Identity | Identity | E |
| Symmetry plane | Reflection in the plane | σ |
| Inversion center | Inversion of a point *x,y,z* to *-x,-y,-z* | i |
| Proper axis | Rotation by (360/n)° | $C_n$ |
| Improper axis | 1. Rotation by (360/n)°<br>2. Reflection in plane perpendicular to rotation axis | $S_n$ |

8

7

# SYMMETRY OPERATIONS

**Reflection** **Rotation** **Inversion** **Rotation-Inversion**



# Rotation

## Proper rotation ($C_n$ or n)

$$\varphi = \frac{360}{n}$$

n = fold of axis

| | |
|---|---|
| 1 | $\varphi = 360^o$ |
| 2 | $\varphi = 180^o$ |
| 3 | $\varphi = 120^o$ |
| 4 | $\varphi = 90^o$ |
| 6 | $\varphi = 60^o$ |

***Why only 5 rotoaxis ?***

# *Minimum symmetry criteria*

| | |
|---|---|
| **Cubic** | **Four 3 or fold rotation axes** |
| **Tetragonal** | **One 4-fold rotation axis** |
| **Orthorhombic** | **Three 2-fold rotation axes** |
| **Rhombohedral** | **One 3-fold rotation axis** |
| **Hexagonal** | **One 6-fold rotation axis** |
| **Monoclinic** | **One 2-fold rotation axis** |
| **Triclinic** | **None** |

## Rotation and Rotation

**Two rotation operation a point generates a third rotation axis**

**Orientations of rotation axes:** **Euler Construction**

$$\cos A = \frac{\cos \beta/2 \bullet \cos \gamma/2 + \cos \alpha/2}{\sin \beta/2 \bullet \sin \gamma/2}$$

Where A is angle between first rotation axes with throw $\beta$ and $\gamma$

e.g. two 2-fold rotation normal to each other gives another 2-fold normal to them

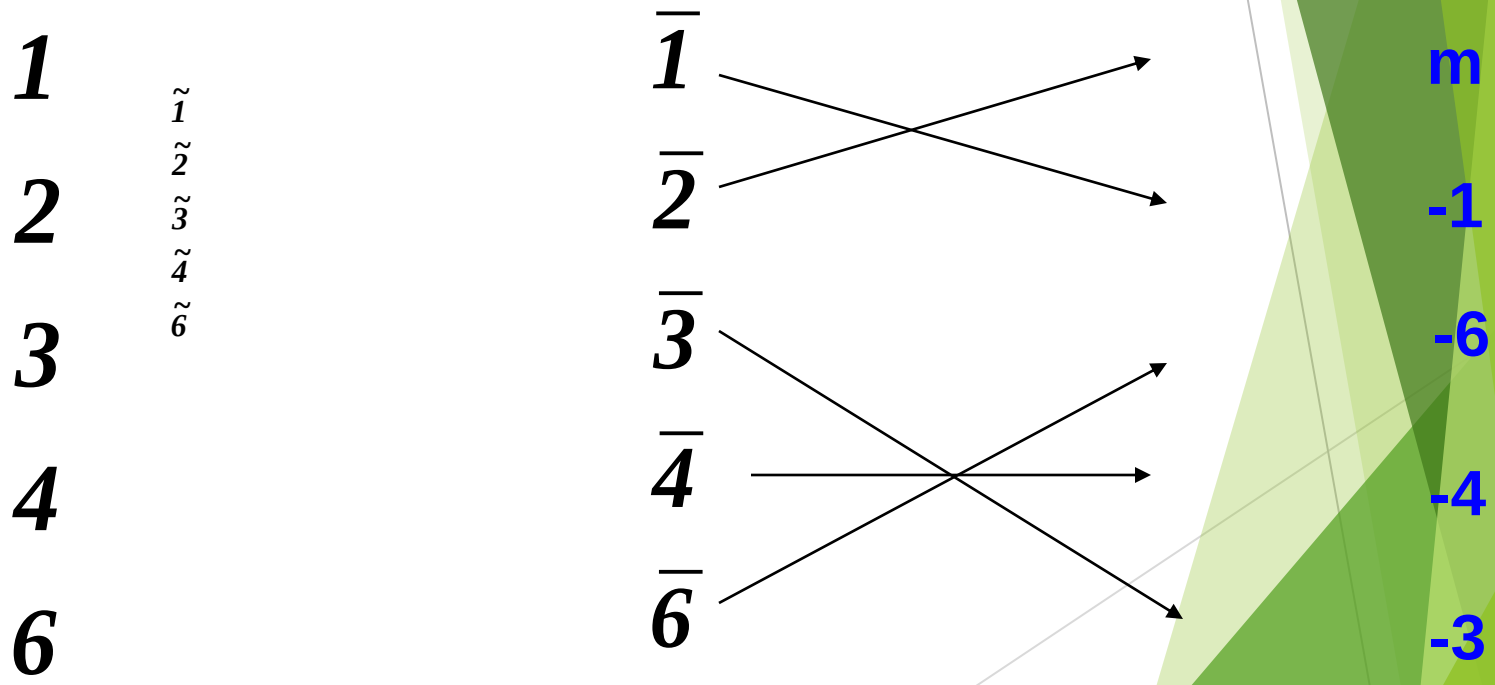
**2•2=2**

# *Rotation and reflection*

**Proper rotation**

**Improper rotation**

**Rotoinversion** **Rotoreflection**



# Notations

| | | | |
|---|---|---|---|
| Rotation | | | X |
| Inversion | | | $\bar{X}$ |
| Rotation | Diad normal to R | | X2 |
| Rotation | | Planes parallel to R | Xm |
| Inversion | Diad normal to R | | $\bar{X}$2 |
| Inversion | | Planes parallel to R | $\bar{X}$m |
| Rotation | | Planes parallel to R and planes normal to R | X/mm ($\frac{X}{m}m$) |

# Point Groups

| System | | | Centric | | | | Centric |
|---|---|---|---|---|---|---|---|
| Triclinic | 1 | | $\bar{1}$ | | | | |
| Monoclinic | 2 | m | $\frac{2}{m}$ | | | | |
| orthorhombic | 222 | mm2 | mmm $(\frac{2}{m}\frac{2}{m}\frac{2}{m})$ | | | | |
| Tetragonal | 4 | $\bar{4}$ | $\frac{4}{m}$ | 422 | 4mm | $\bar{4}2m$ | 4/mmm $\frac{4}{m}\frac{2}{m}\frac{2}{m}$ |
| Rhombohedral | 3 | | $\bar{3}$ | 32 | 3m | | $\bar{3}m$ |
| Hexagonal | 6 | $\bar{6}$ | $\frac{6}{m}$ | 622 | 6mm | $\bar{6}m2$ | 6/mmm $\frac{6}{m}\frac{2}{m}\frac{2}{m}$ |
| Cubic | 23 | | m3 $\frac{2}{m}\bar{3}$ | | 432 | $\bar{4}3m$ | m3m $\frac{4}{m}\bar{3}\frac{2}{m}$ |

## Point Group

distinguishable symmetries operations around a point

2D Lattices – 10 distinct Point Groups

3D Lattices – 32 distinct Point Groups

## Space Group

distinguishable symmetries operations of a crystal lattice
(translational symmetry in addition to all points groups)

2D Lattices – 17 distinct Space Groups

3D Lattices – 230 distinct Space Groups

# Rotation and translation

**Translation: Primitive**
**Non primitive**

| Proper rotation | | Screw |
|---|---|---|
| $1$ | | |
| $2$ | $\frac{1}{2}t$ | $2_1$ |
| $3$ | $\frac{1}{3}t, \frac{2}{3}t$ | $3_1, 3_2$ |
| $4$ | $\frac{1}{4}t, \frac{2}{4}t, \frac{3}{4}t$ | $4_1, 4_2, 4_3$ |
| $6$ | $\frac{1}{6}t, \frac{2}{6}t, \frac{3}{6}t, \frac{4}{6}t, \frac{5}{6}t$ | $6_1, 6_2, 6_3, 6_4, 6_5$ |

# *Reflection and translation*

| Symbol | Symmetry plane | translation |
|---|---|---|
| a | axial glide | a/2 along [100] |
| b | axial glide | b/2 along [010] |
| c | axial glide | c/2 along [001]<br>along [111] in rhombohedral |
| n | diagonal | (a+b)/2, or (b+c)/2 or (c+a)/2<br><br>(a+b+c)/2 (in tetra and cube) |
| d | diamond | (a±b)/4, or (b±c)/4 or (c±a)/4<br><br>(a±b±c)/4 (in tetra and cube) |

**32 Point Groups + 14 Bravais Lattices**

**230 Space Groups**

**ALL CRYSTALLINE MATTER BELONGS TO ONE OF THE 230 SPACE GROUPS**

# Space group notations

| System | Space group as in Int. Tab. | | |
|---|---|---|---|
| | 1 | 2 | 3 |
| Triclinic | No special | | |
| Monoclinic | 2 or -2 along b (unique b-axis) | | |
| Orthorhombic | 2 or -2 along a | 2 or -2 along b | 2 or -2 along c |
| Tetragonal | 4 or -4 along c | 2 or -2 along a and b | 2 or -2 along [110] |
| Trigonal | 3 or -3 along c | 2 or -2 along a, b and [110] | 2 or -2 normalto a, b and [110] |
| Hexagonal | 6 or -6 along c | 2 or -2 along a, b and [110] | 2 or -2 normal to a, b and [110] |
| Cubic | 4 or -4 along a, b and c | 3 or -3 along <111> | 2 or -2 along <110> |

# Law of crystallography

## Law of constant interfacial angle

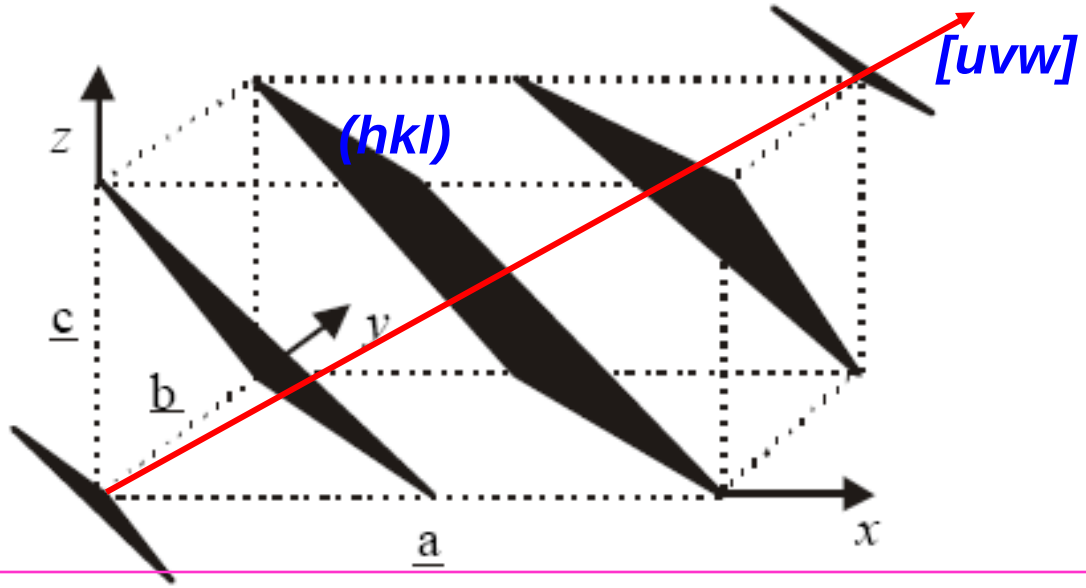
- Angle between two planes of a crystal do not change with species and size
- Habit of crystal remains same in natural crystal growth

## Law of rational indices

$$hu + kv + lw = constant$$

- Orientation of a plane in a given direction and direction of a plane defined by ***h:k:l*** and ***u:v:w*** ratios
- The ratios ***h:k:l*** of all planes and ratios ***u:v:w*** of all directions are rational number

# Crystallographic Planes and directions

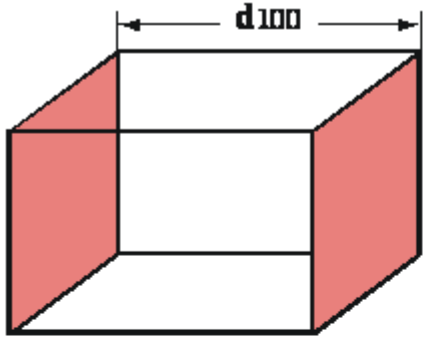



**Find intercept of plane in term of cell lengths**
**Take reciprocals**
**Clear fractions**

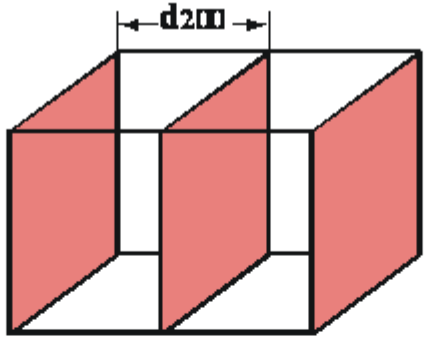
Miller indices of plane (h k l) and directions [u v w]

***(h, k, l) defines sets of equally spaced parallel planes***

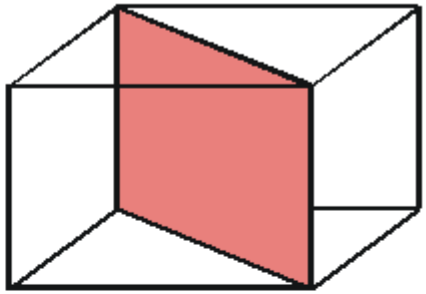
# Lattice Planes



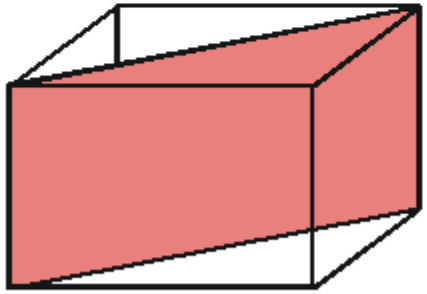

(100)



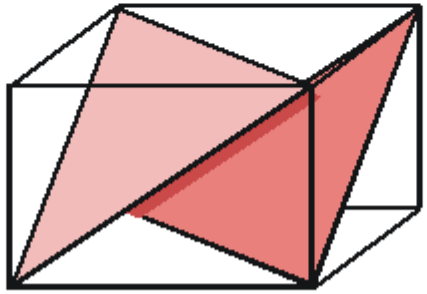

(200)



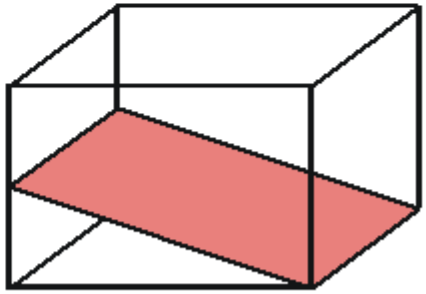
(110)



($\bar{1}10$)



($11\bar{1}$)

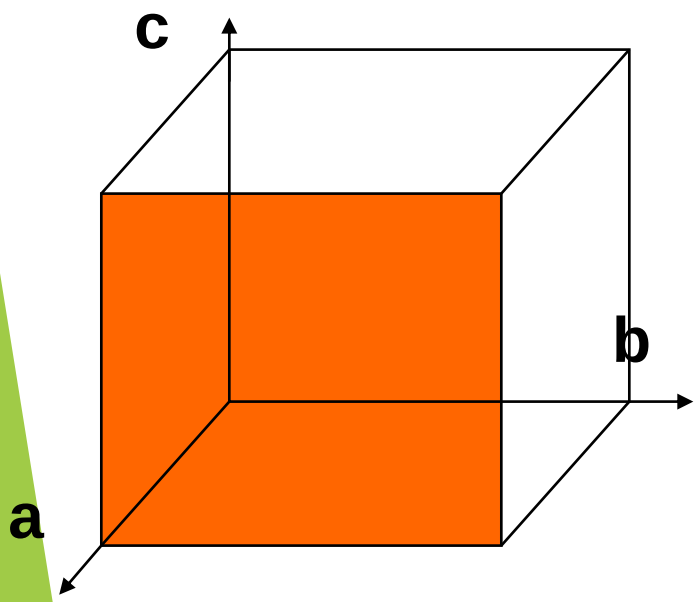


(102)

# Miller indices of a family of planes and directions

{h k l}

- ***Planes with equal interplanar spacing (d)***
- ***The miller indices can be interchanged***
- ***All possible combinations of positive and negative values***



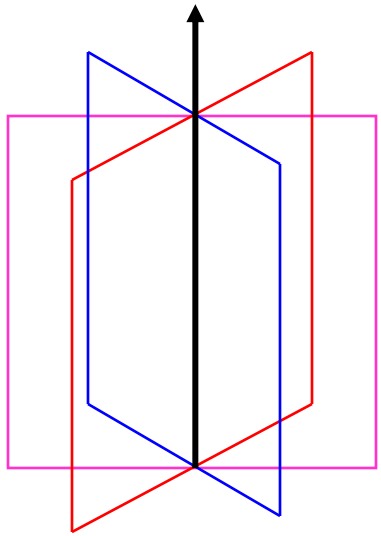

| In a cube | |
|---|---|
| Family | No. of planes |
| {100} | 6 |
| {110} | 12 |
| {111} | 8 |

<u v w> ***Set of directions with symmetrically equal orientation, e.g. cube edges***

# *(Zone axis)*

## *Common direction of planes*

***[uvw]***



$h_1u+k_1v+l_1w = const.$

$h_2u+k_2v+l_2w = const.$

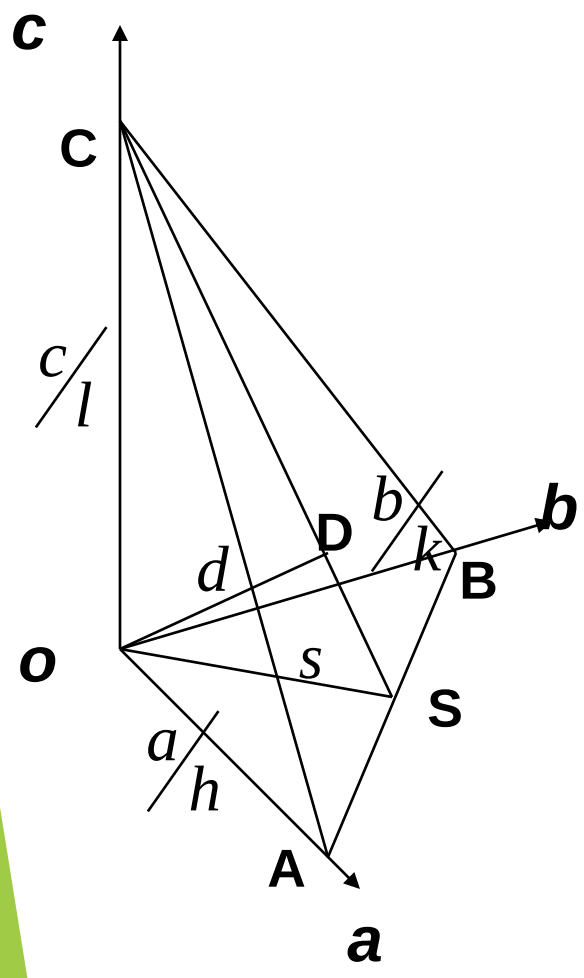
$u = k_1l_2-k_2l_1$

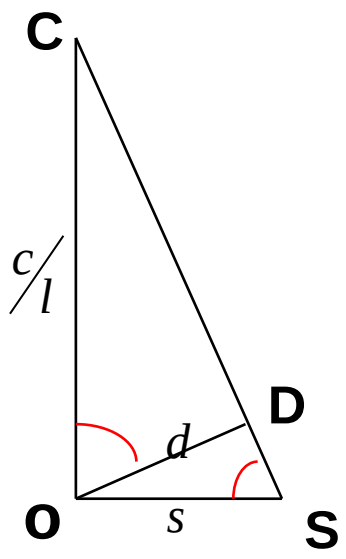
$v = h_2l_1-h_1l_2$

$w = k_1k_2-h_2k_1$

# Unit cell parameters and interplanar spacing

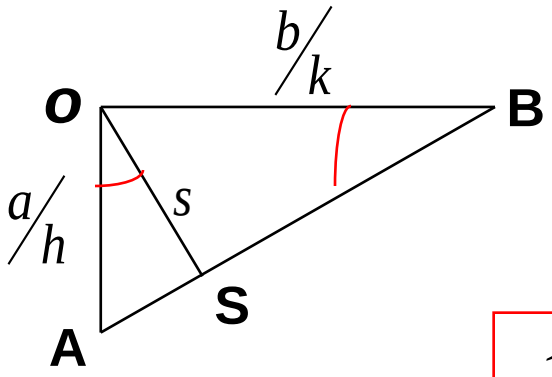
## Orthorhombic system




triangle SOC and SDO

$$\frac{OS}{OD} = \frac{SC}{OC}$$




triangle AOB and ASO

$$\frac{OA}{OS} = \frac{AB}{OB}$$

$$\frac{1}{d^2} = \frac{a^2}{h^2} + \frac{b^2}{k^2} + \frac{c^2}{l^2}$$

# Unit cell parameters and interplanar spacing

## Triclinic system

$$\frac{1}{d^2}=\frac{\frac{h^2}{a^2}Sin^2\alpha+\frac{k^2}{b^2}Sin^2\beta+\frac{l^2}{c^2}Sin^2\gamma+\frac{2hk}{ab}\left(Cos\alpha\cdot Cos\beta-Cos\gamma\right)+\frac{2kl}{bc}\left(Cos\beta\cdot Cos\gamma-Cos\alpha\right)+\frac{2lh}{ca}\left(Cos\gamma\cdot Cos\alpha-Cos\beta\right)}{1-Cos^2\alpha-Cos^2\beta-Cos^2\gamma+2Cos\alpha\cdot Cos\beta\cdot Cos\gamma}$$

$$V^2=a^2b^2c^2\left(1-Cos^2\alpha-Cos^2\beta-Cos^2\gamma+2Cos\alpha\cdot Cos\beta\cdot Cos\gamma\right)$$

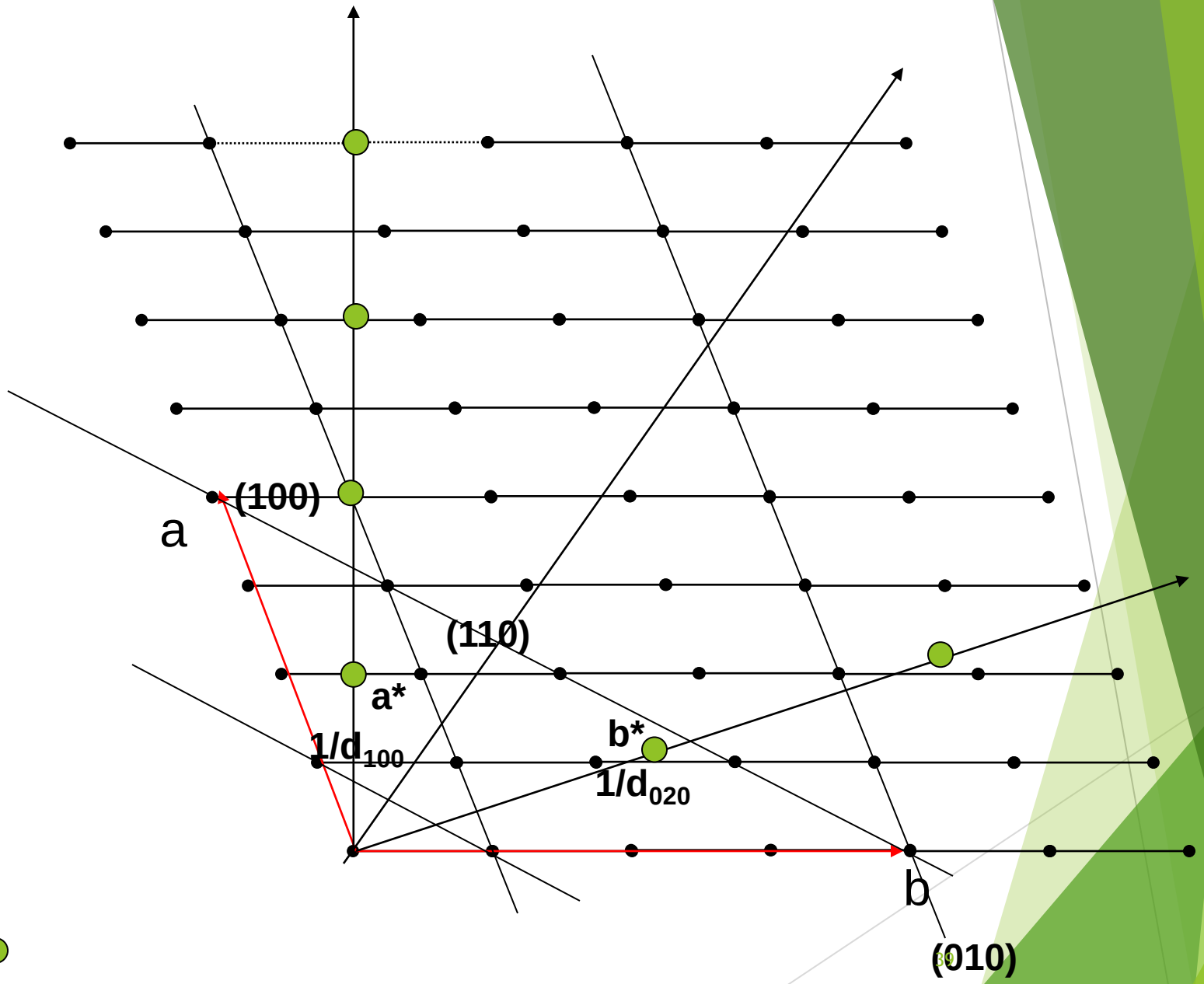
$$\frac{1}{d^2}=h^2\left(a^*\right)^2+k^2\left(b^*\right)^2+l^2\left(c^*\right)^2+2hka^*b^*Cos\gamma^*+2klb^*c^*Cos\alpha^*+2lhc^*a^*Cos\beta^*$$

# Reciprocal lattice

**Imaginary (hypothetical) lattice but bears direct correspondence with diffraction data**

**Lattice points indicates the planes of direct lattice**

**Unit cell parameters have $Å^{-1}$ units**


(100)
a
(110)
a*
1/d100
b*
1/d020
b
(010)

# Reciprocal to direct lattice relation

$$a^* = \frac{b \times c}{V} = \frac{b \times c}{a \cdot b \times c}$$

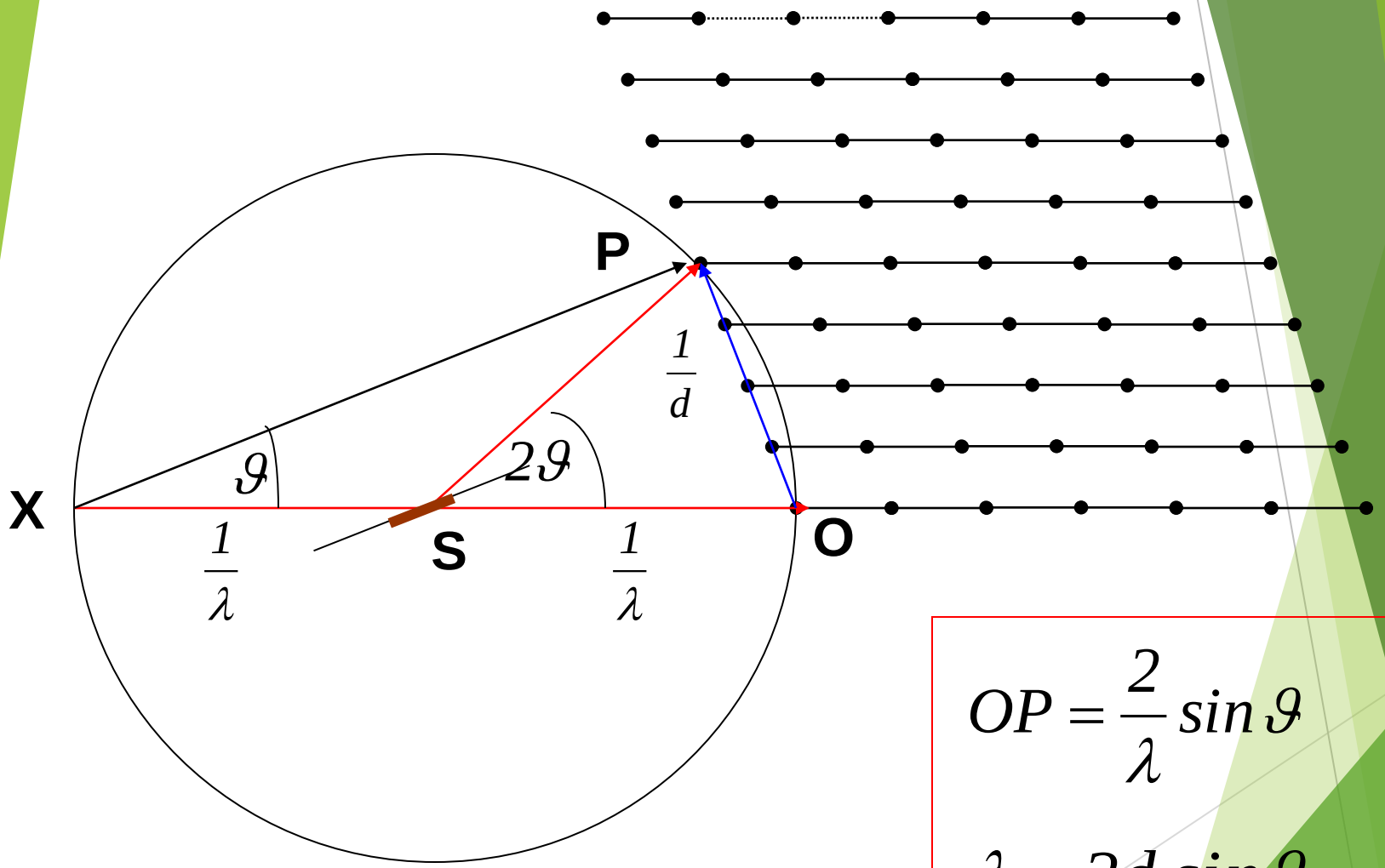
$$b^* = \frac{c \times a}{V} = \frac{c \times a}{a \cdot b \times c}$$

$$c^* = \frac{a \times b}{V} = \frac{a \times b}{a \cdot b \times c}$$

$$\cos\alpha^* = \frac{\cos\beta \cdot \cos\gamma - \cos\alpha}{\sin\beta \cdot \sin\gamma}$$

$$\cos\beta^* = \frac{\cos\gamma \cdot \cos\alpha - \cos\beta}{\sin\lambda \cdot \sin\alpha}$$

$$\cos\gamma^* = \frac{\cos\alpha \cdot \cos\beta - \cos\gamma}{\sin\alpha \cdot \sin\beta}$$

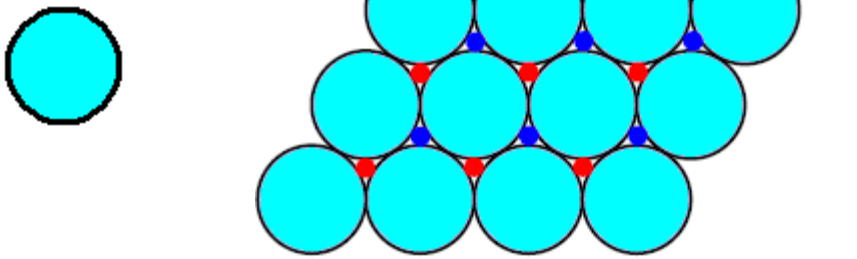



$$OP = \frac{2}{\lambda} \sin\vartheta$$

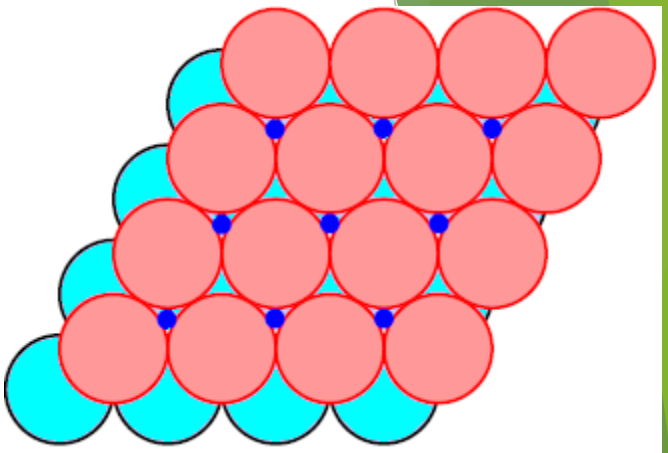
$$\lambda = 2d \sin\vartheta$$

- Structure of solids
- HCP and CCP
- Holes and space filling

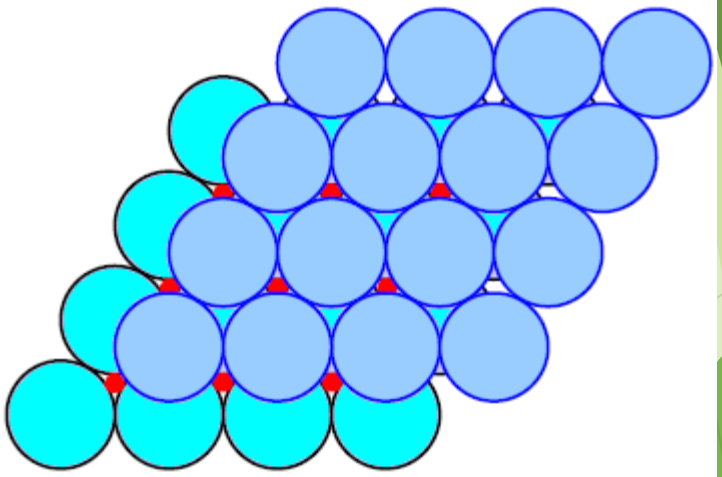
# Close Packing



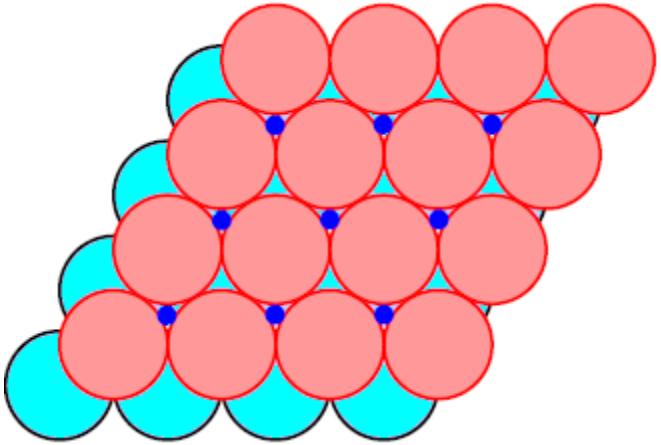
B C



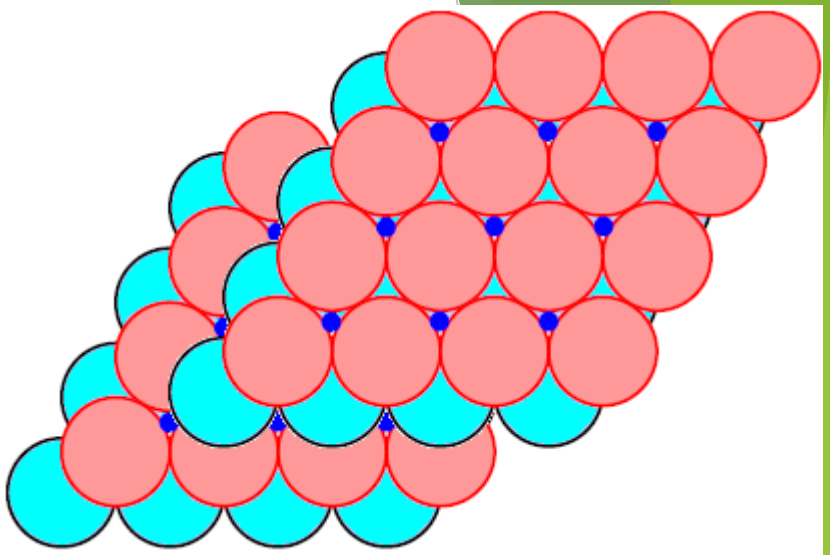
AB



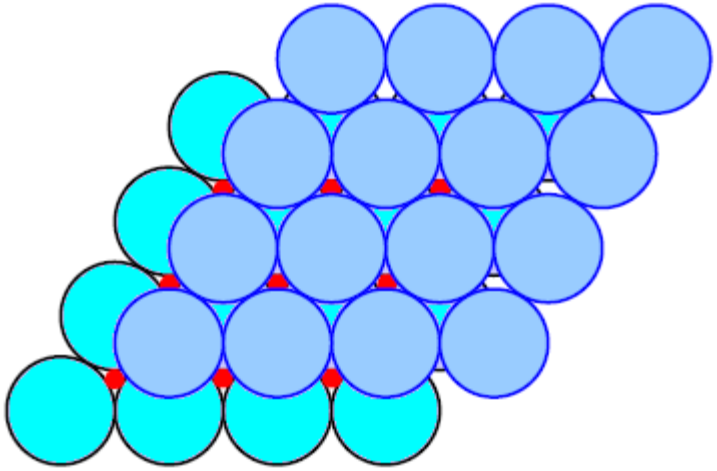
AC



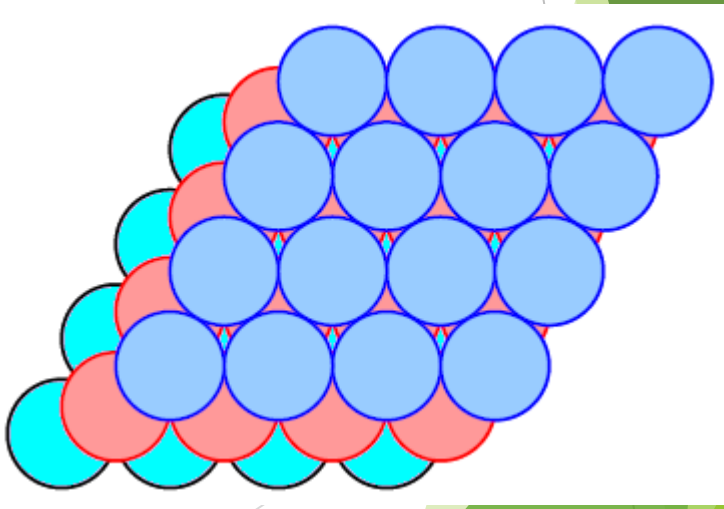
AB



ABAB *(hcp)*

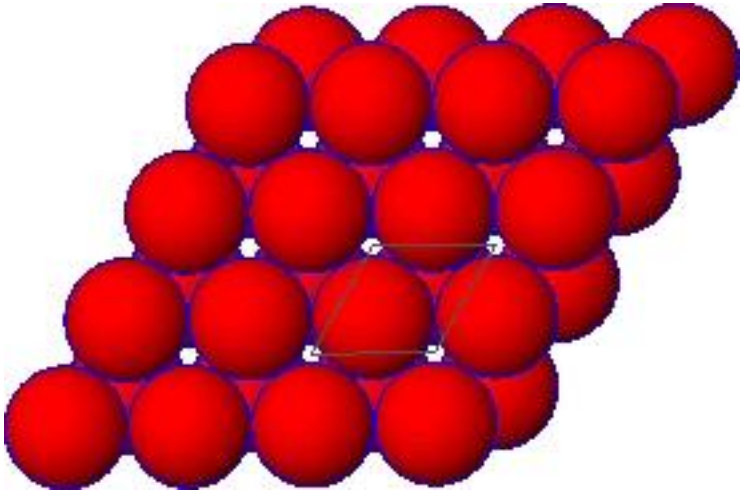


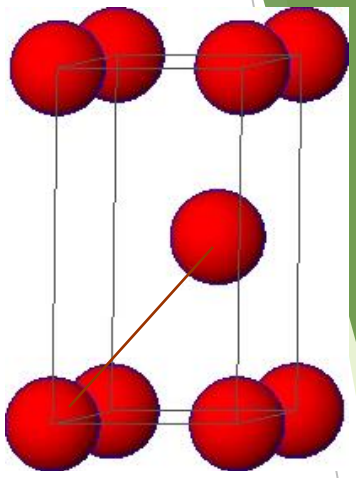
AB



ABC *(ccp)*

# ABAB *(hcp)*

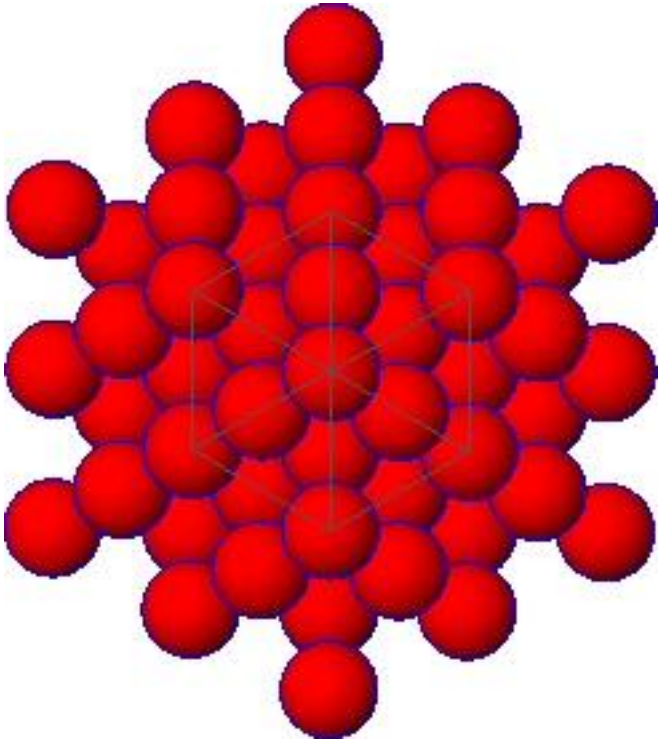


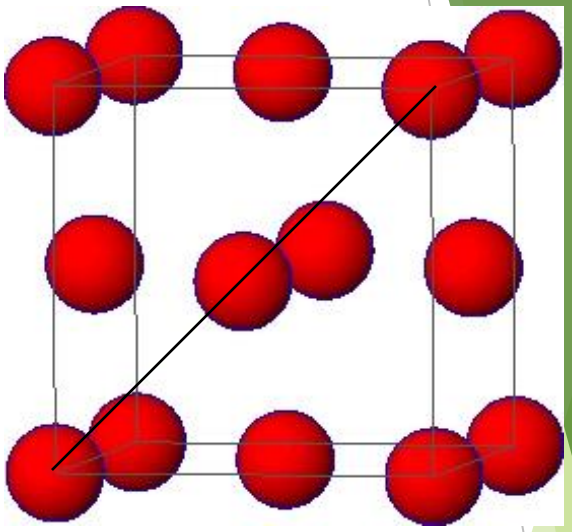


$P6_3/mmc$
**a** = 2 (r)
**c/a** = $\sqrt{(8/3)}$ = 1.633
M *2c*: 1/3 2/3 1/4
r = sphere radius

CN = 12
Packing fraction = 74%

# ABC *(ccp)*





Fm3m

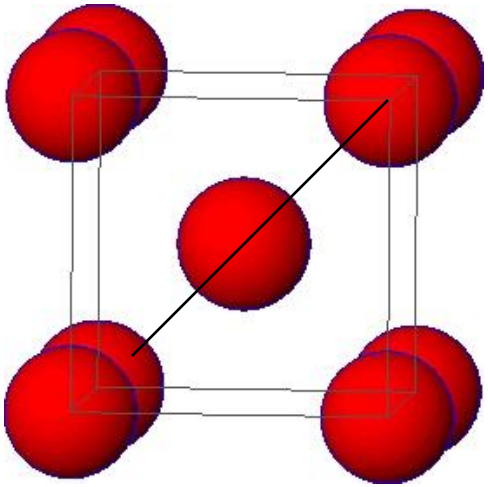
**a** = 4r/ $\sqrt{2}$

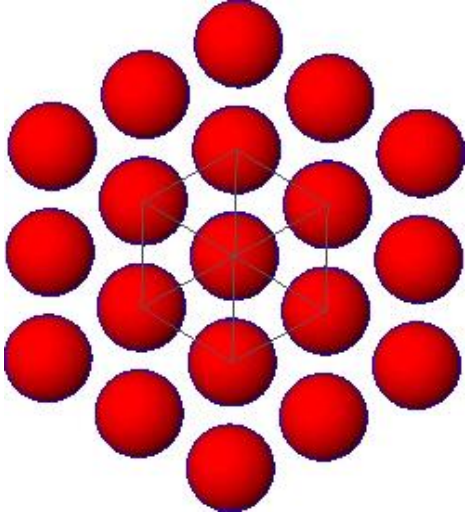
M 4a 0 0 0

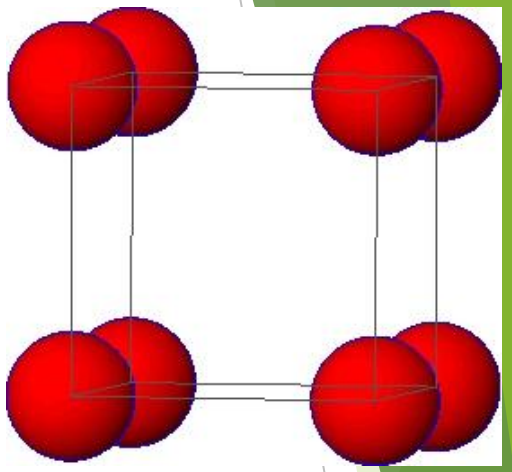
r = Sphere radius

CN = 12

Packing fraction = 74%







Im3m

**a** = 4r/√3

M *2a* : 0 0 0

r = Sphere radius

CN = 8

Packing fraction = 68%

Pm3m

**a** = 2 r

M *2a* : 0 0 0

r = Sphere radius

CN = 8

Packing fraction = 52%



Packing fraction in diamond cube = 34%

# Pauling's rule

1. Coordination polyhedron

   Anions surround the cations in a definte coordination polyhedron depending radius sum and radius ratio

2. Charge balance (bond balance sum rule)

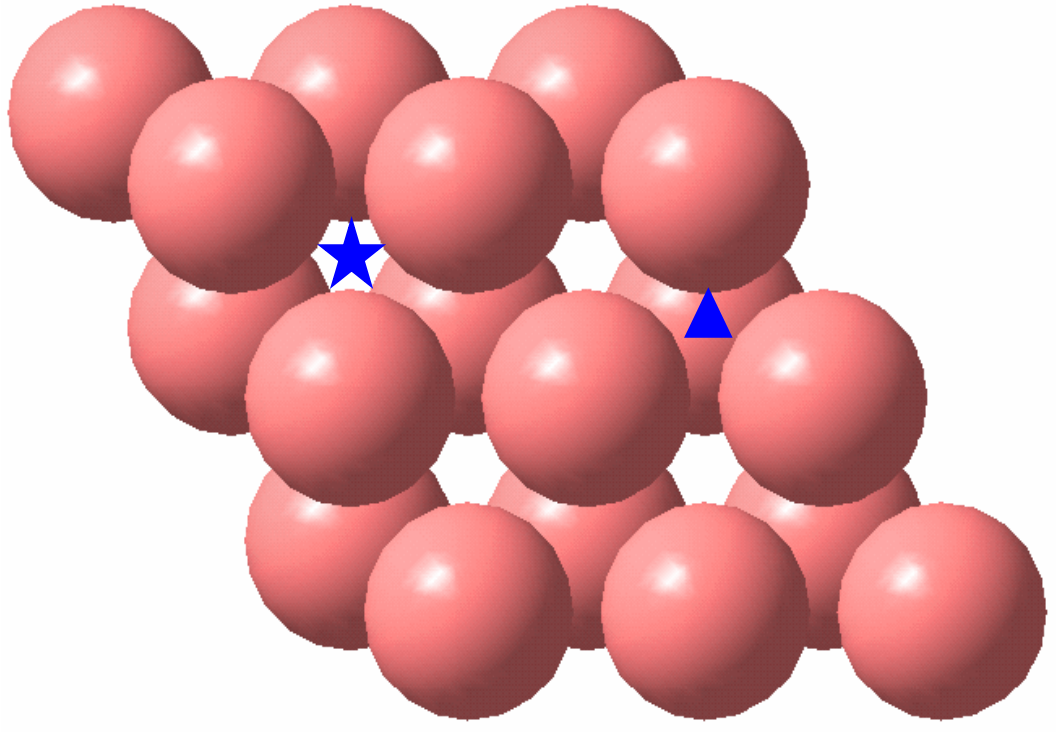
   Valence reaches to anion is equal to charge of anion

3. Sharing of polyhedra

   Highly charged cations do not prefer share face and edges

4. More symmetric arrangements

   Less number of distingushable atoms are preferred



In hcp or ccp: The octahedral and tetrahedral holes are empty
octhedral hole : tetrahedral hole : Sphere = 1:2:1

***Size of oh hole:***
***0.424 r***

***Size of td hole:***
***0.225 r***

# *Space fillings*

radius ratio rule

| $r_c/r_a$ | CN | Configuration |
|---|---|---|
| 0.0-0.155 | 2 | Linear |
| 0.155-0.225 | 3 | triangular |
| 0.225-0.414 | 4 | tetrahedral |
| 0.414-0.732 | 6 | octehedral |
| 0.732-1.0 | 8 | cube |
| 1.0 | 12 | ccp/hcp |

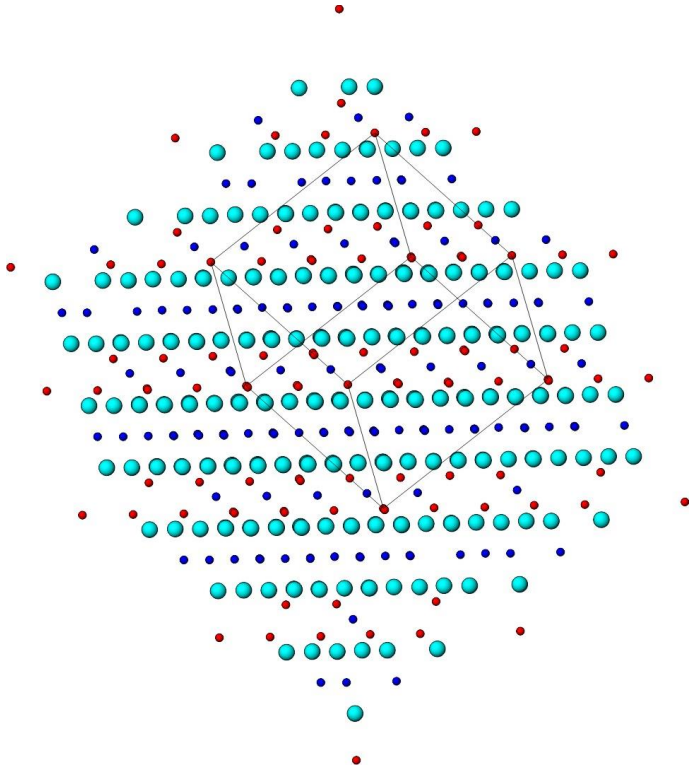
# Description of Crystal Structure

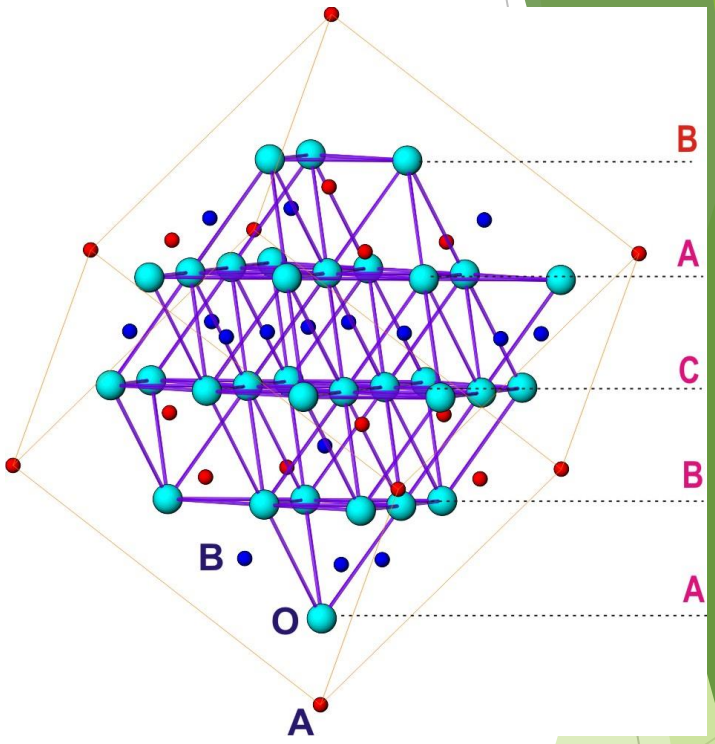
- **Specification of Crystal Lattice :**
  **sizes, type, crystal system**

- **Specification of Basis :**
  **fractional co-ordinates of atoms**

# $AB_2X_4$ (Spinel)

Anions stacked as fcc sequence
1/2 of the octahedral holes occupied by B
1/8$^{th}$ of terahedral holes are occupied by A



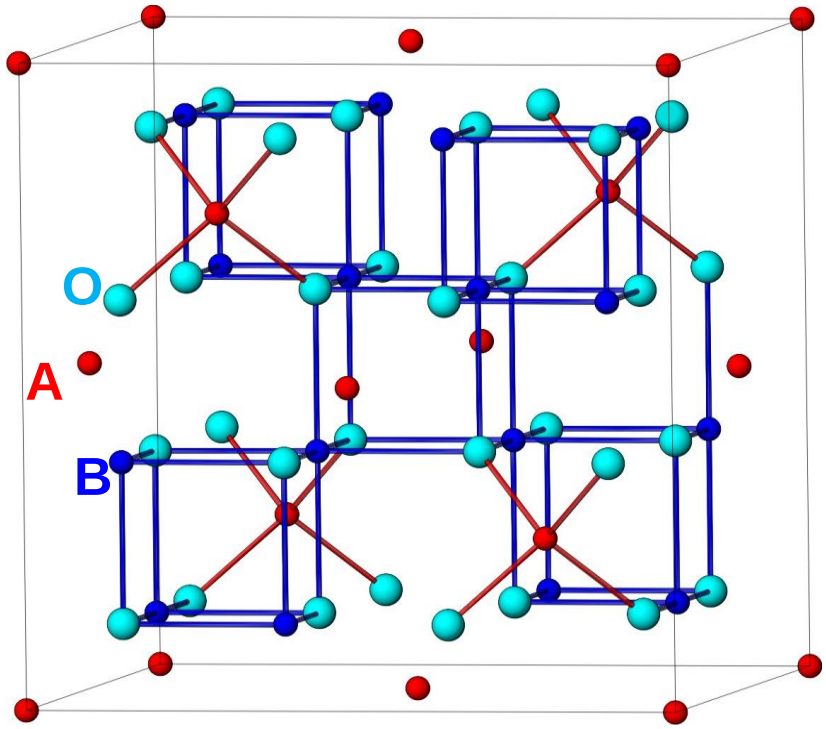



**A (0,0,0) = Tetrahedral cation**

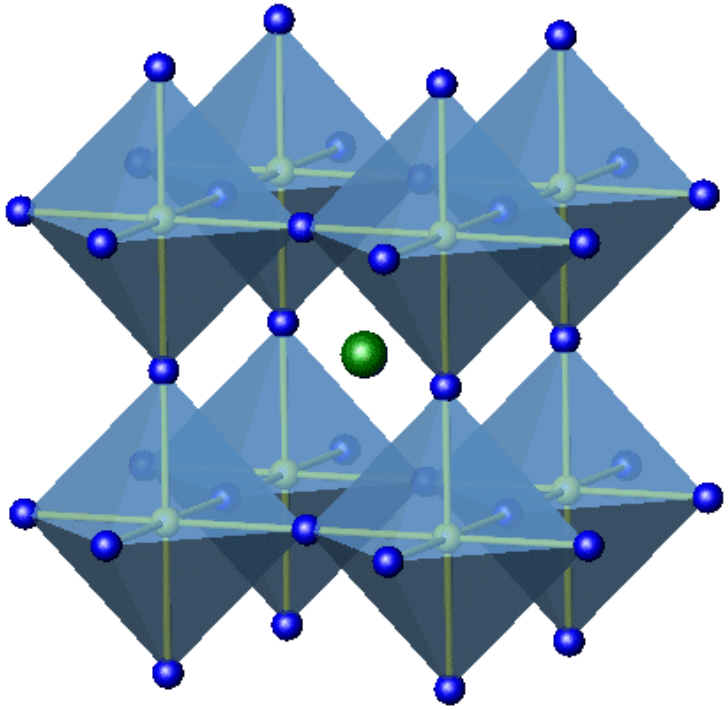
**B (5/8,5/8,5/8) = Octahedral cation**

**X (x,x,x) = anion (x ~ 0.375)**

a ~ 8-10 Å
SG: Fd3m


O
A
B

# $ABX_3$ (perovskites)



**A (1/2,1/2,1/2) = large cation (CN=12)**
**(alkali, alkali-earth, rare-earth)**

**B (0,0,0) = small cation (CN=6)**

**X (0,0,1/2) = anion ($O^{2-}$, $F^-$)**

a ~ 3.8-4.2 Å

SG: Pm3m

## Goldsmith's tolerance rule

$$t = (r_A + r_O)/\sqrt{2}(r_B + r_O)$$

t = 1 - undistorted cubic perovskite

t < 1 - distorted perovskite with tilted $BO_6$ octahedra

t > 1 - hexagonally distorted perovskites

Martin, J. Buerger, “Crystal Structure analysis”,
John Wiley and Sons, New York
Leonid V. Azaroff, “Elements of X-ray crystallography”,
McGraw Hill book company, New York
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H. P. Klug and L. E. Alexander, “X-ray diffraction procedures”,
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L. V. Azaroff, M. J. Buerger, “The powder method in X-ray crystallography”
McGraw-Hill Book Company, NY
A. R. West, “Solid state Chemistry and its Applications”,
John Wiley and Sons, Chichester

*International Tables for Crystallography, IUCr Publications*

# Thank you