Chapter 7

Introduction to Crystallography

Crystalline Substances: e.g., Diamond and Table Salt

Diamonds

7.1 **periodicity and lattices of crystal structure**

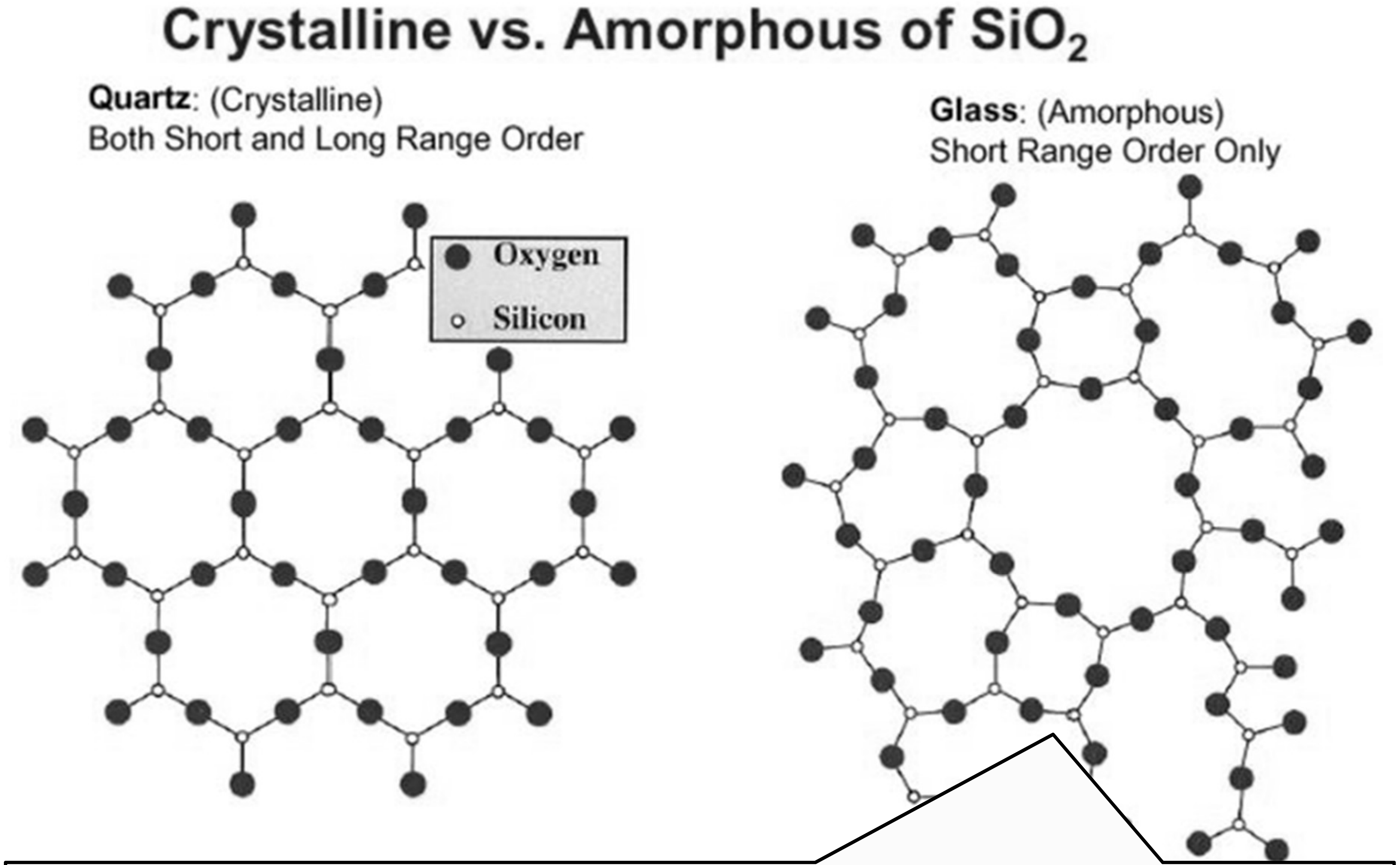
7.1.1 The characteristics of crystal structure

1. A few definitions:

- Solids can be divided into two primary categories, crystalline solids and amorphous solids.
- Crystalline Solids are built from atoms or molecules arranged in a periodic manner in space, e.g., rock salt and diamond.
- Amorphous Solids possess short-range order only. They are not related through symmetry, e.g. glass, rosin, amber glass.

➢ Short-Range Order: Fixed bond lengths and angles
➢ Long-Range Order: Associated with a lattice point

Crystals are solids that are built from atoms or molecules arranged in a periodic manner in space.



C.N.:

Si = 4

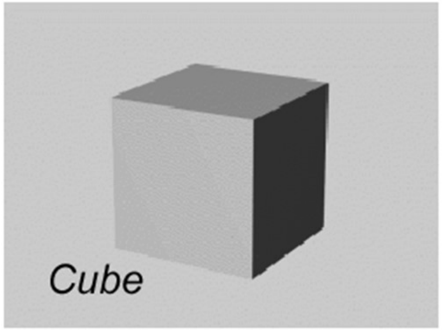
O = 2

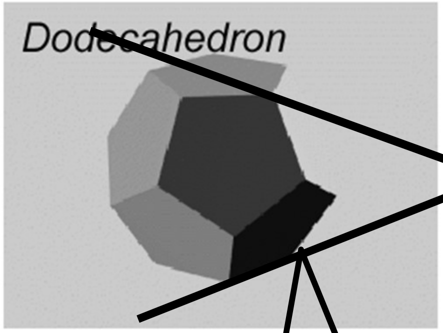
Short range order: fixed bond lengths and angles due to the bonding nature of constituent atoms.

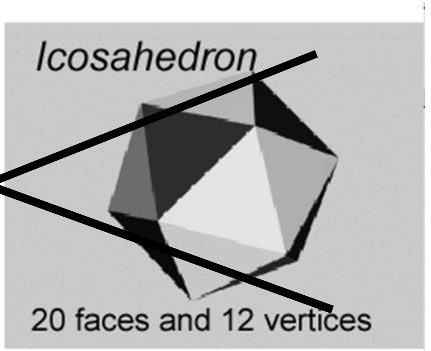
2. Fundamental characteristics of crystal

a) Spontaneous formation of polyhedral shapes

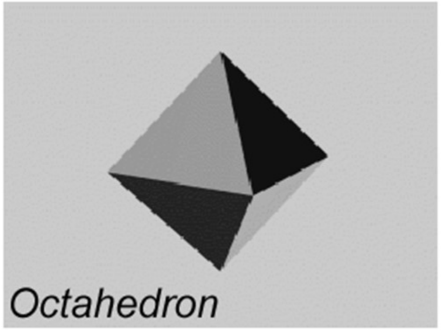
$$\mathbf{F + V = E + 2}$$

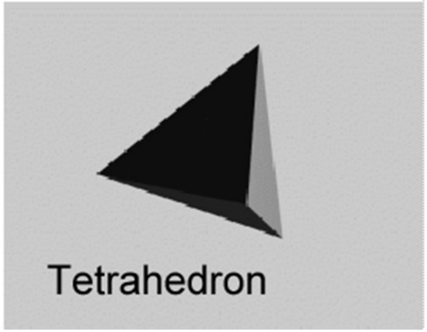




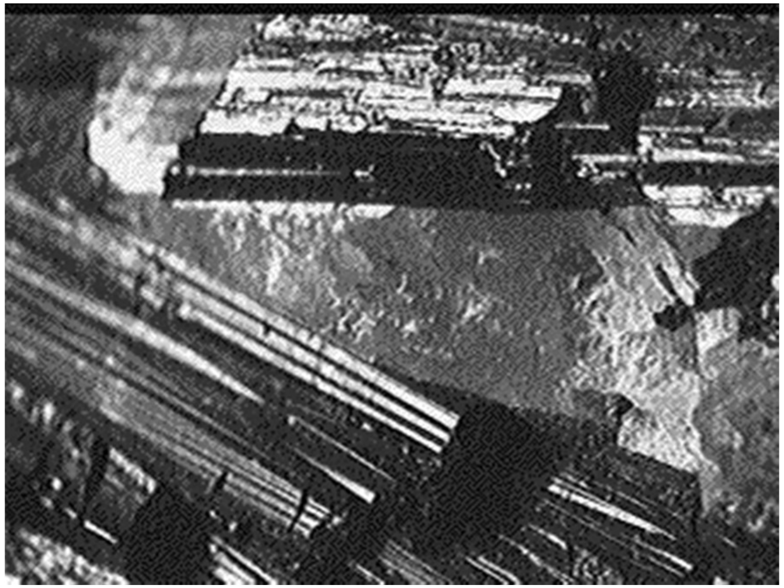


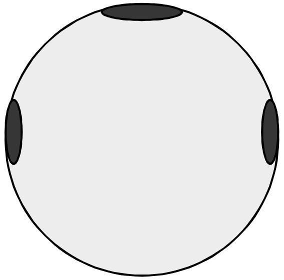
No 5-fold axis is allowed in a single crystal!



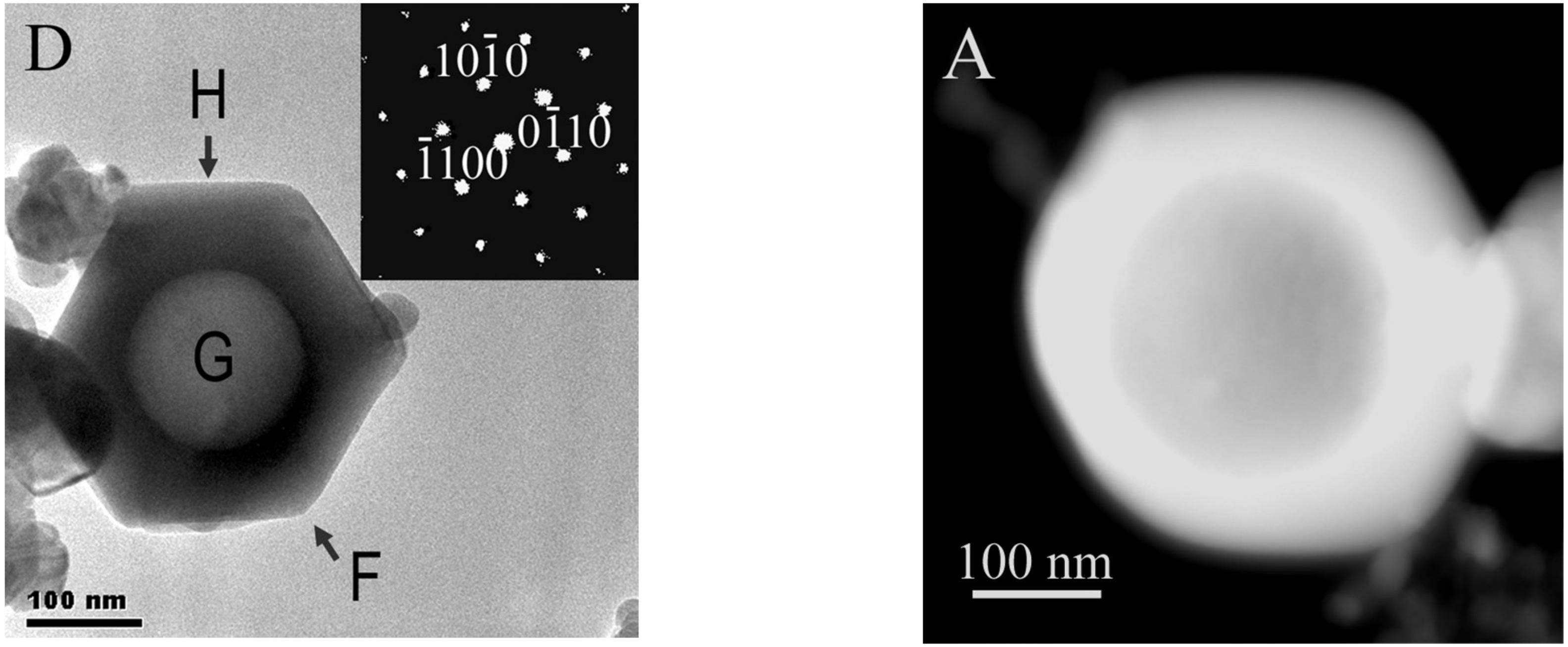


b) Uniformity: periodic distribution of atoms/molecules





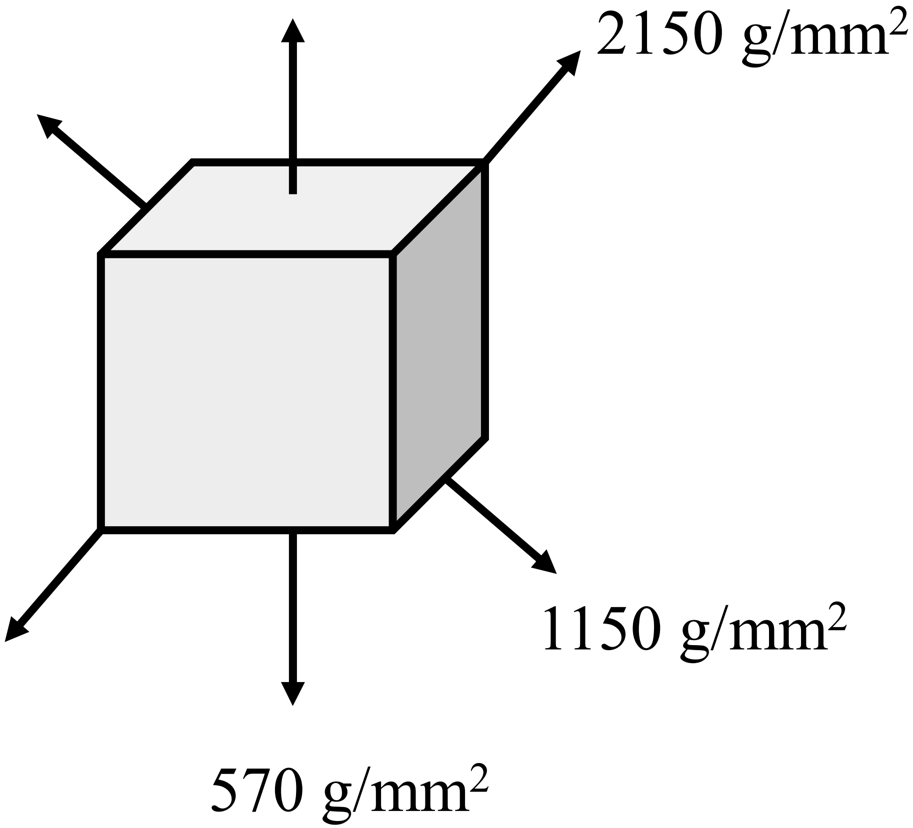
Single crystal gold bead with naturally formed facets



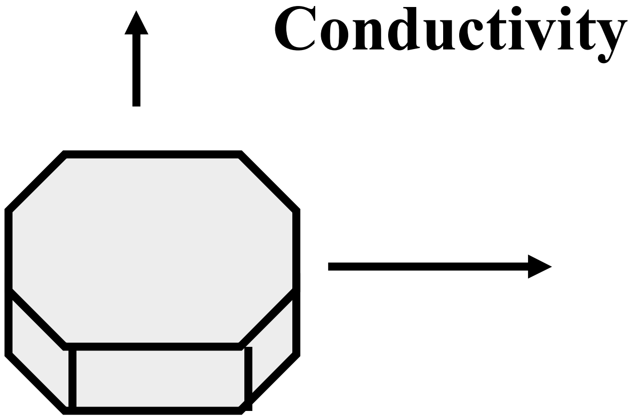
HRTEM images of hollow beads

•Anisotropy

Different periodicity and density for different direction.

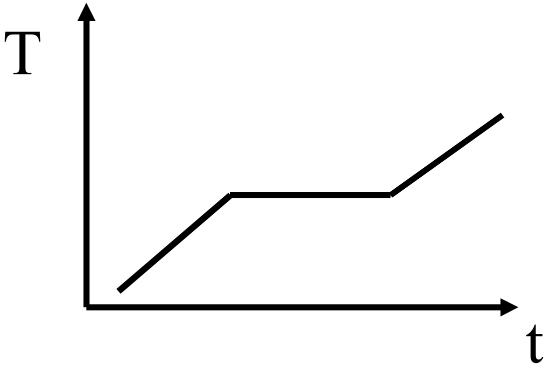


NaCl



Graphite

- Definite sharp melting points

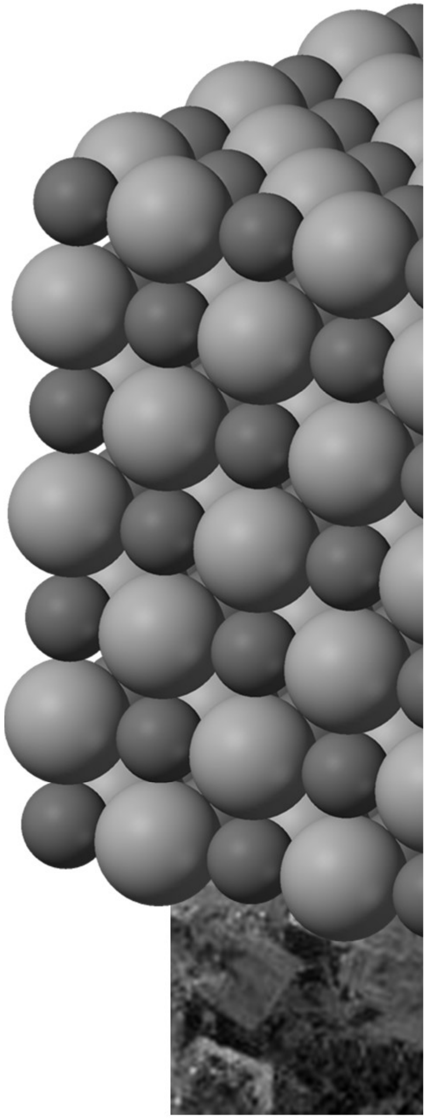


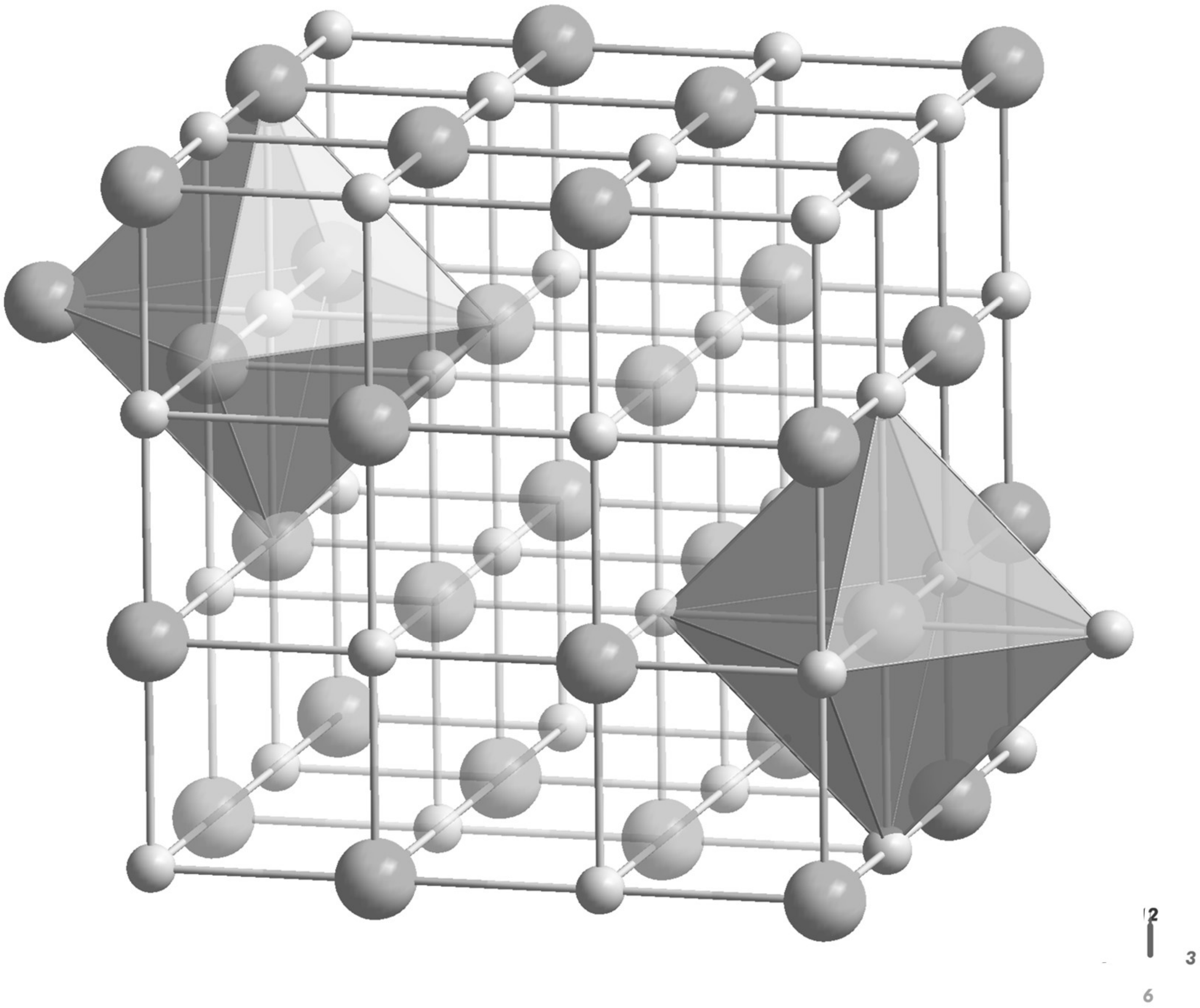
- Symmetry: crystal shape (macroscopic)
  lattice arrangement (microscopic)

- X-ray diffraction by crystals:

  atomic distances match the wavelength of x-ray.

Sodium Chloride: Solid and Crystal structure



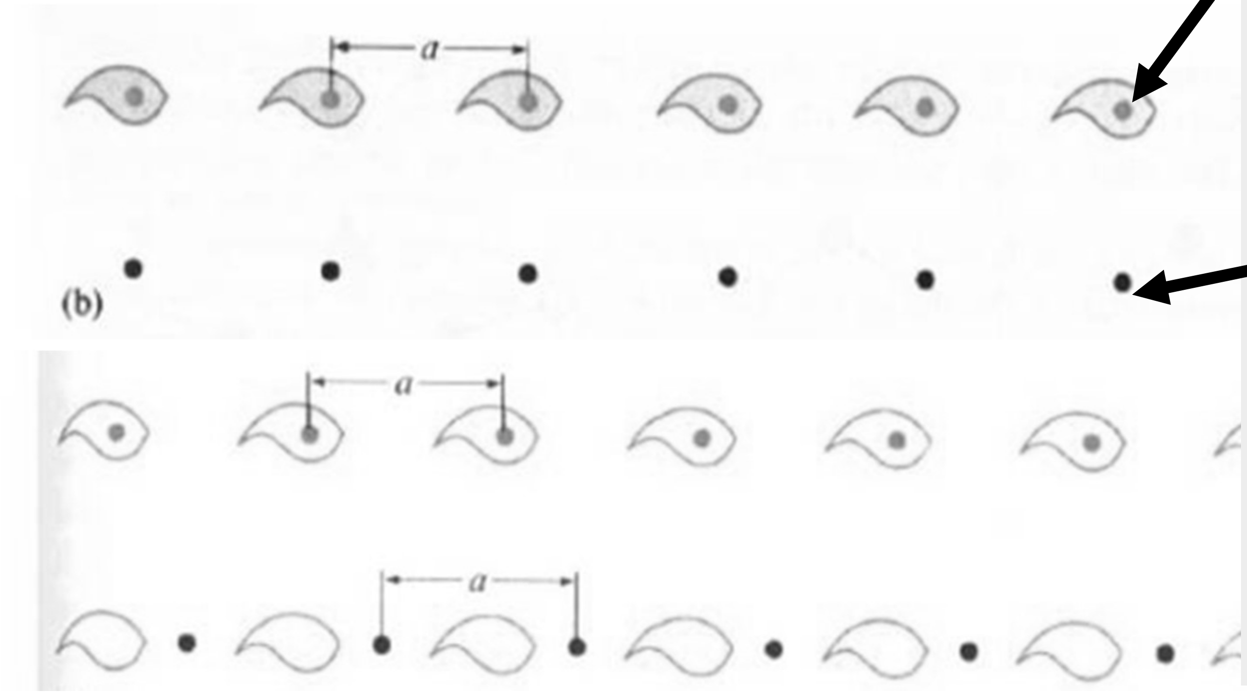


7.1.2 The lattice and unit cell

Lattice:

- A periodic pattern of points in space, such that each lattice point has identical surroundings.
- Can be reproduced by translational motion along the vector between any two points.

a. 1D lattice and its unit:

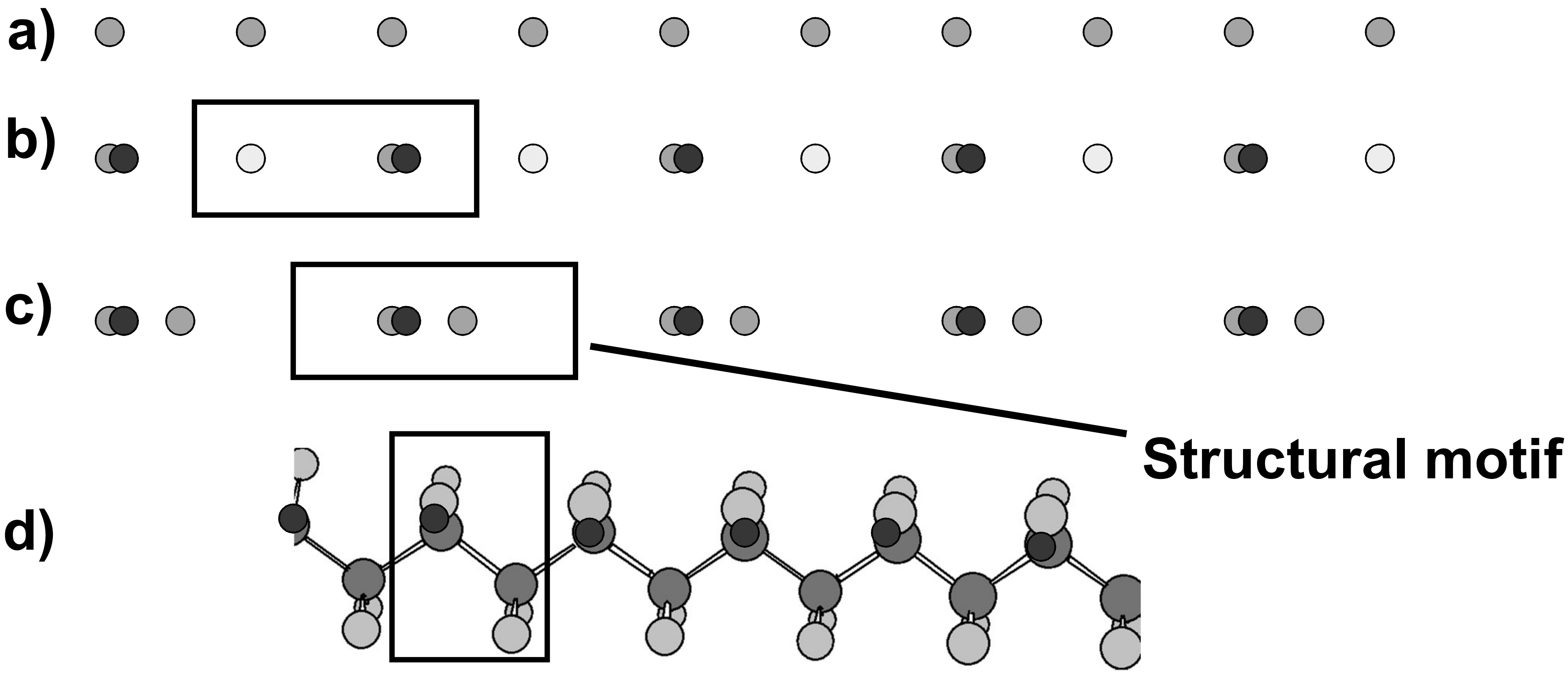


- Each motif in this 1D periodic pattern can be represented by a point.
- A lattice of repeating points is thus obtained to represent the above 1D system.

- The translation vectors connecting any two lattice points constitute a translation group. i.e.,

$$\mathbf{T}_\mathbf{m} = m\boldsymbol{a} \quad (m = 0, \pm 1, \pm 2, \ldots, \pm\infty) \qquad \boldsymbol{a}\text{: basic vector.}$$

Examples of 1D lattice



a is a 1D lattice itself;

b-d are not lattices, but can be represented by a lattice.

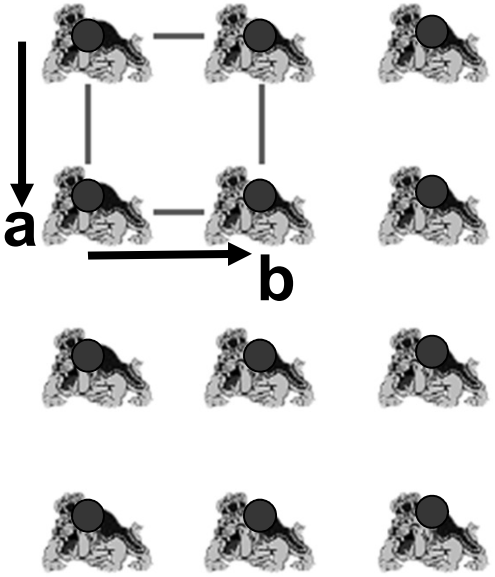
A pattern with periodicity = a lattice + structural motif!

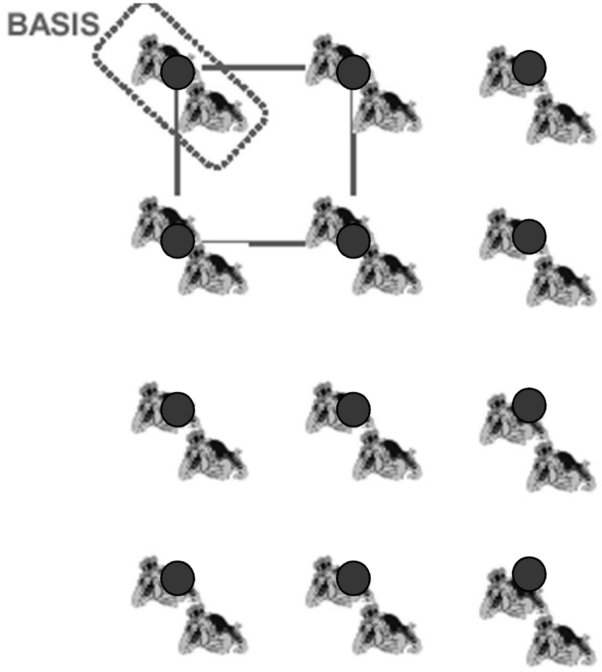
b. Lattice and its unit in 2D:

$\mathbf{T}_{mn} = m\underline{\boldsymbol{a}} + n\underline{\boldsymbol{b}}$ （m, n = 0,±1, ± 2， …)

a & ***b***: independent basic vectors

$\{\mathbf{T}_{mn}\}$ – a translation group

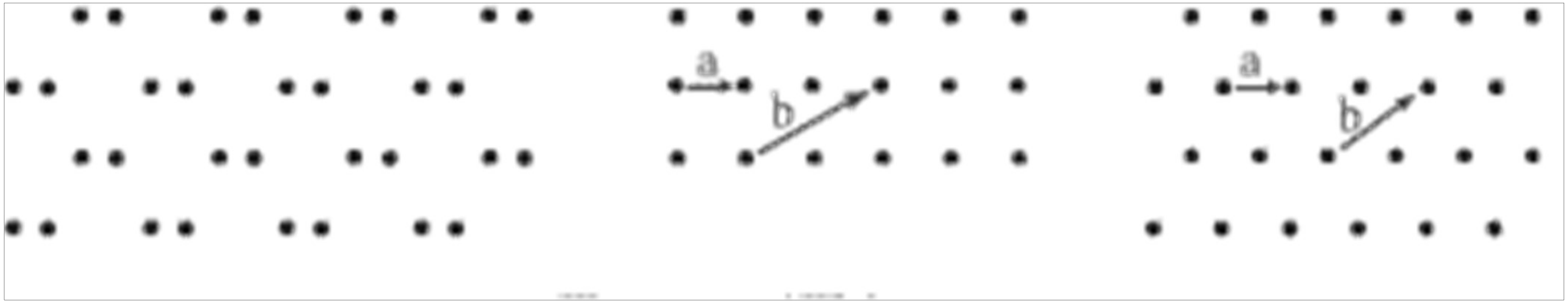




- Crystal structure = lattice + structural motif (basis)

Lattice:

- A periodic pattern of points in space, such that each lattice point has identical surroundings.
- Can be reproduced by translational motion along the vector between any two points.

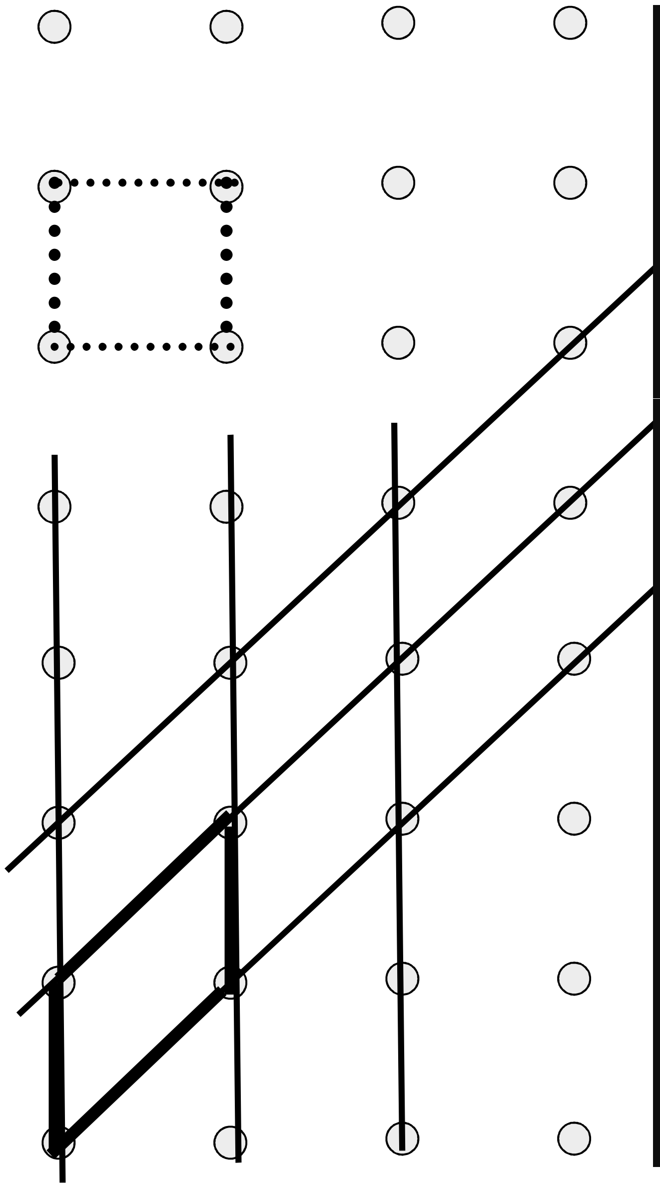


This 2D pattern itself is not a lattice, but can be represented by a 2D Lattice.

2D lattice.

2D lattice.

2D Primitive Cell



Choice of Unit Cell

- There is always more than one possible choice of unit cell.
- By convention, the chosen unit cell should be as small as possible while reflecting the full symmetry of the lattice.

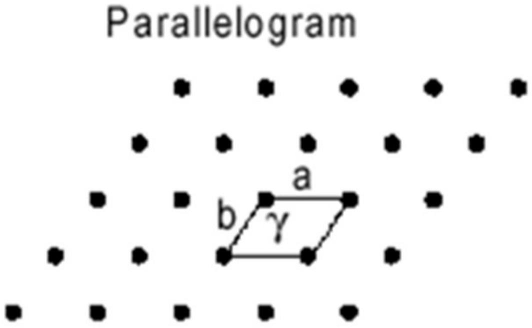
1) The highest symmetry

2) The smallest area (or volume)

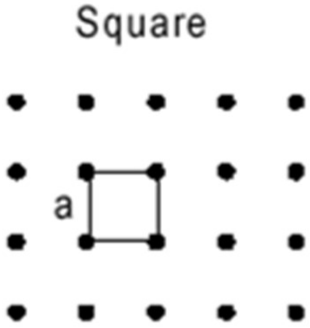
Five types of 2D lattices

There are literally thousands of crystalline materials, there are only 5 distinct planar lattices.

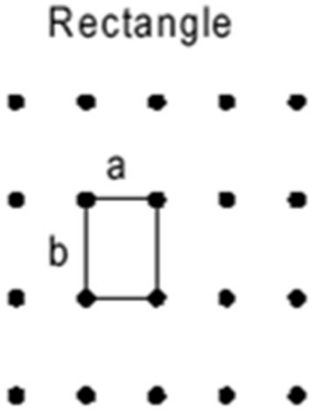
γ-angle between two basic vectors.



a≠b, $\gamma \neq 90°$ & $\gamma \neq 120°$ i



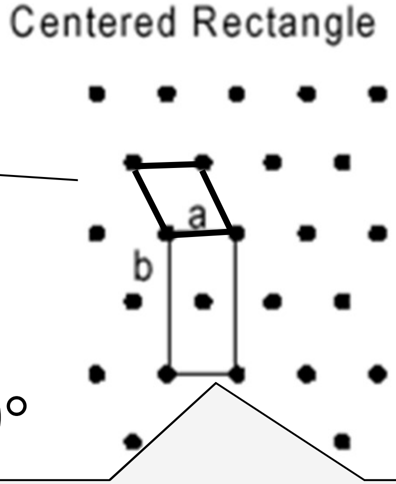
a=b, γ=90° i, C_4



a≠b, γ=90° i, C_2

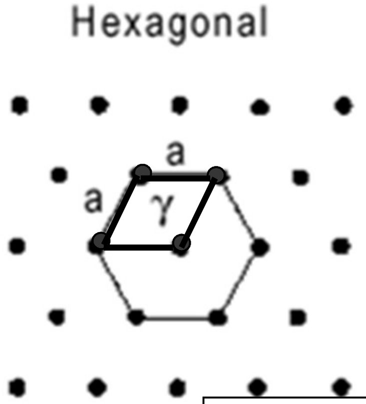
i) Primitive

ii) Centered



a≠b, γ=90°

Centred cell: i + C_2 // Primiative cell: i



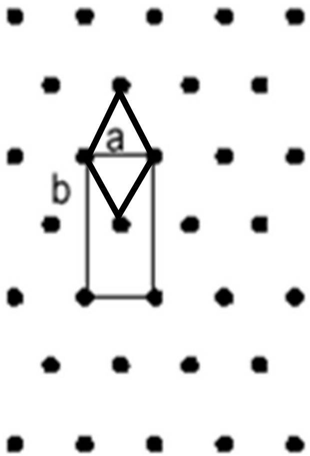
a=b, γ=120° i, C_6

Question:

Both the centred rectangular and simple hexagonal 2D lattices have a rhombic primitive unit cell. What is the key difference between them?

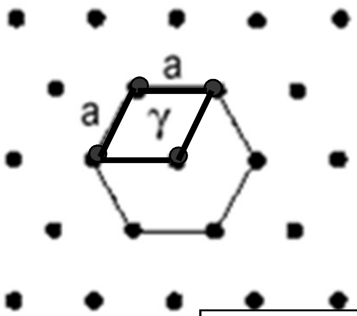
Centered Rectangle

$a \neq b$, $\gamma = 90°$

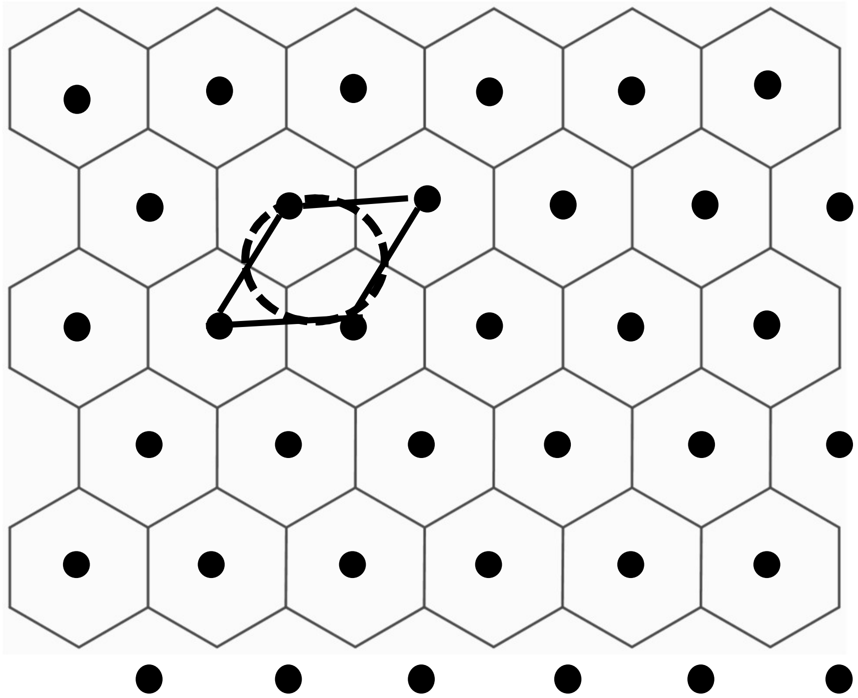


Hexagonal

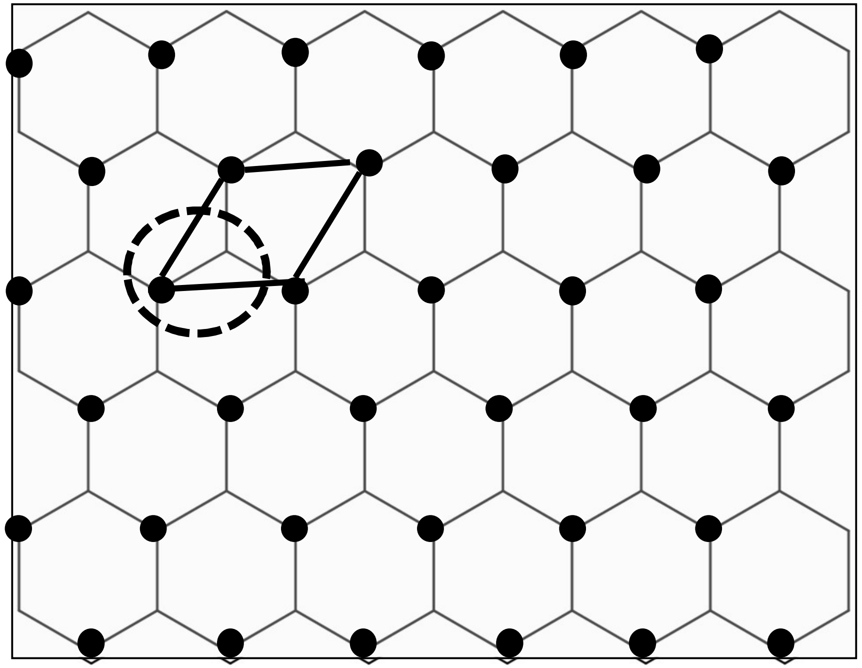
$a = b$, $\gamma = 120°$



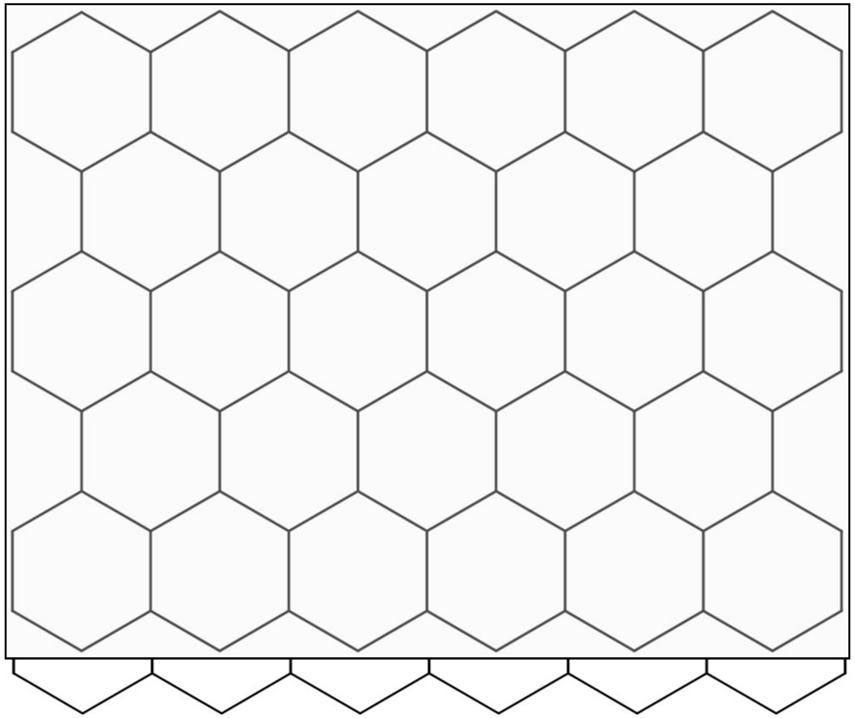
Example: 2D-lattice of Graphene



or

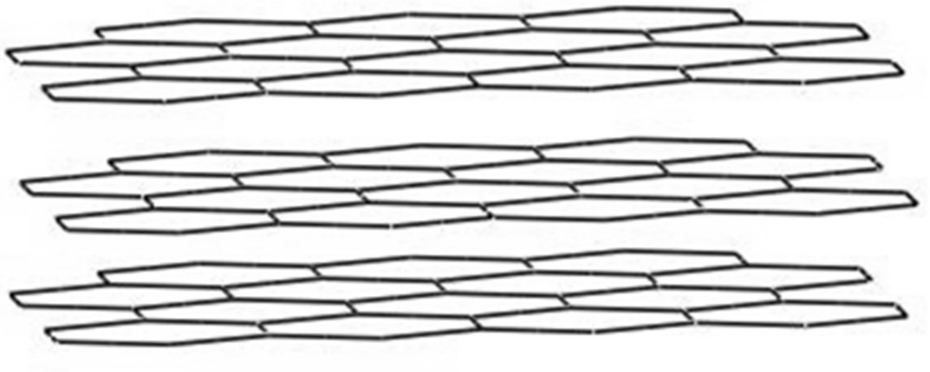


- What's the smallest structure motif of a graphene sheet?
- What type of lattice does a planar graphene sheet belong to?



stacking

graphite



3-D lattice can be used!

c. Lattices and its unit in 3D:

$$T = m\underline{a} + n\underline{b} + p\underline{c}\ \ (m, n, p = 0, \pm 1, \pm 2, \ldots)$$

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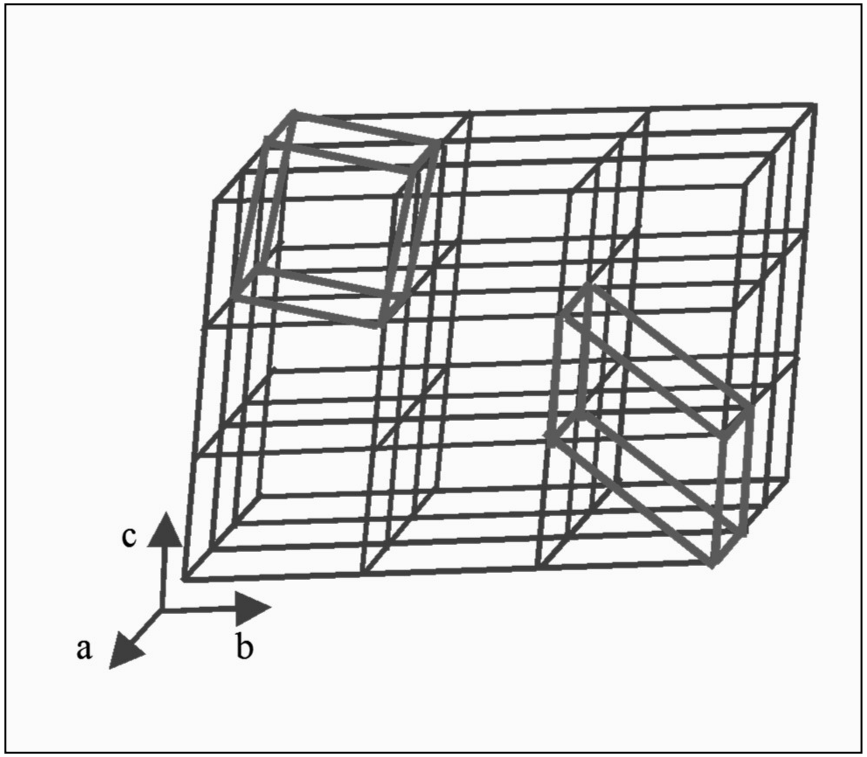
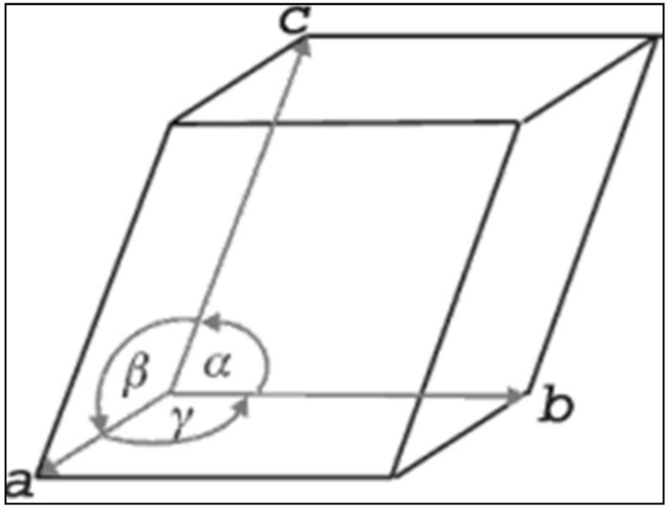
$$T = m\underline{a} + n\underline{b} + p\underline{c} \quad (m, n, p = 0, \pm 1, \pm 2, \ldots)$$

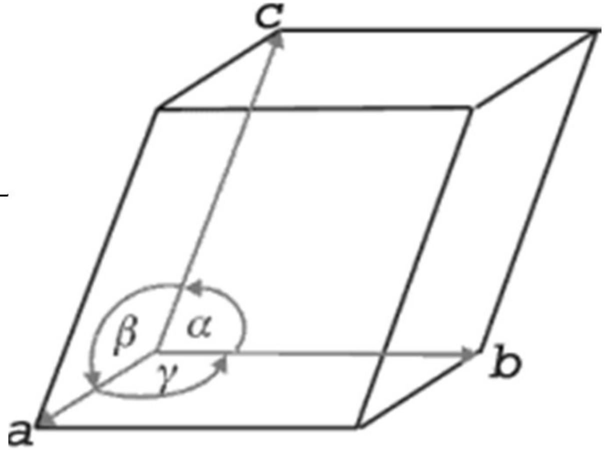




The Choice of a Unit Cell:

Having the highest symmetry and minimal size

The Choice of a Primitive Cell



1) The axial system consisting of the basis vectors should be right handed.

2) The basis vectors should coincide as much as possible with directions of the highest symmetry.

3) Should be the smallest volume that satisfies condition **2**.

4) Of all lattice vectors none is shorter than ***a***.

5) Of those not directed along ***a*** none is shorter than ***b***.

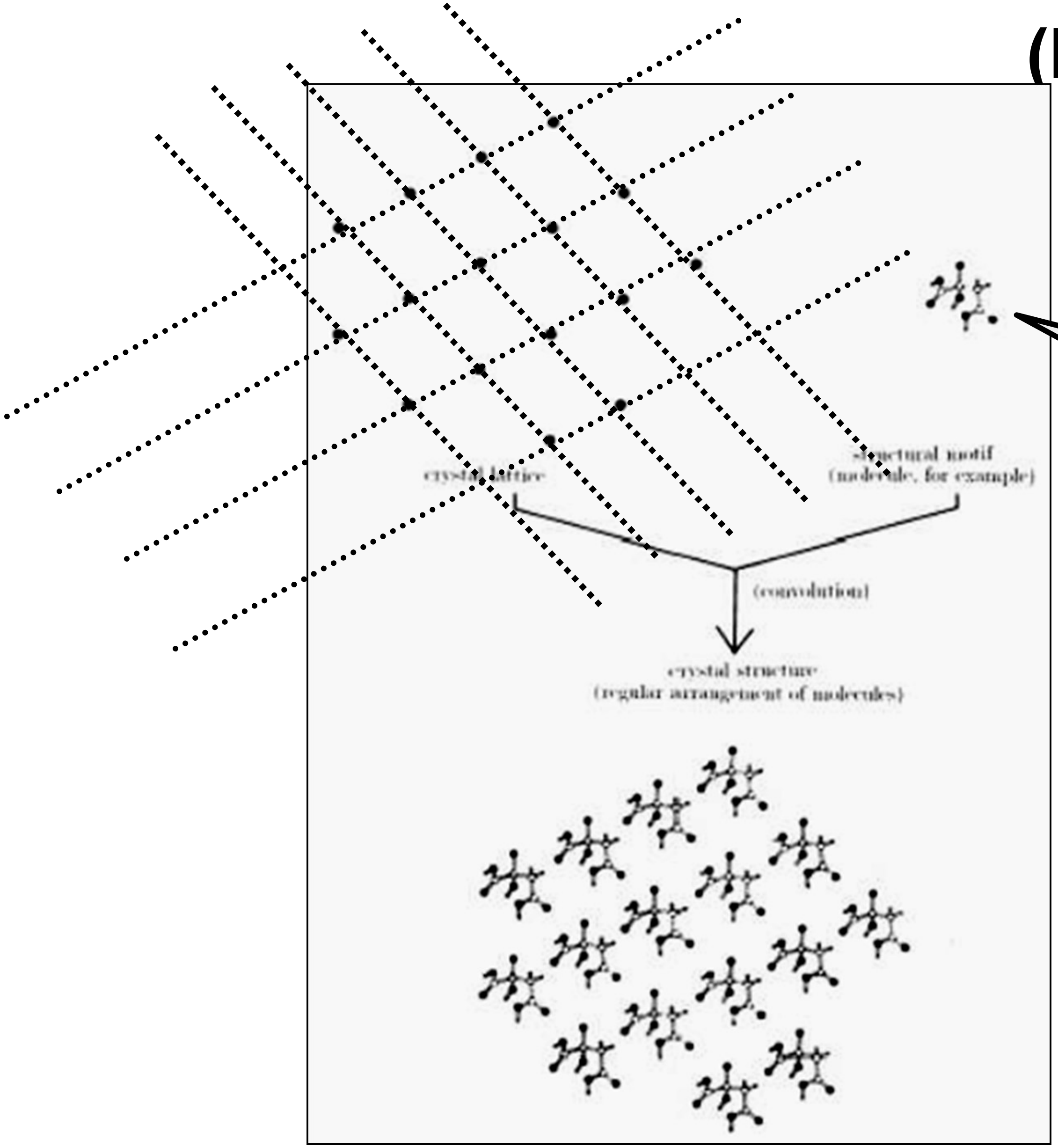
6) Of those not lying in the ***a***, ***b*** plane none is shorter than ***c***.

7) The three angles between the basis vectors ***a,b,c*** are either all acute or obtuse.

Conditions 4-6 define $|\vec{a}| \le |\vec{b}| \le |\vec{c}|$

Crystal structure = lattice + structural motif

(basis)

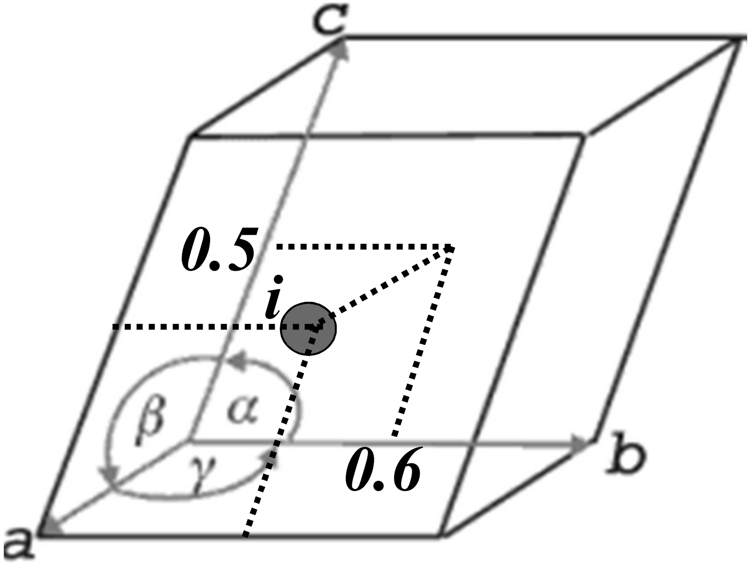


Structural motif

Atomic Coordinates: Fractional coordinates

Fractional coordinates:

- **The positions of atoms inside a unit cell are specified using fractional coordinates *(x,y,z)*.**
- **These coordinates specify the position as fractions of the unit cell edge lengths.**



***i*: (1.0, 0.6, 0.5)**

Example:

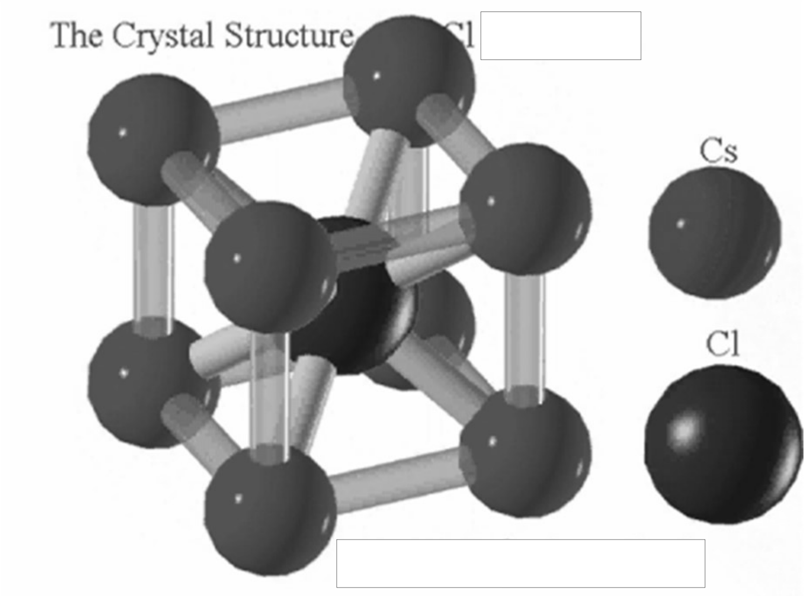
Cubic unit cell of CsCl,

$a=b=c$

$\alpha=\beta=\gamma=90°$

Cs:(0,0,0)

Cl: (1/2,1/2,1/2)



In this case, the lattice point can be put at the position of either Cs or Cl atom. Each unit cell contains both a Cs and Cl atom.

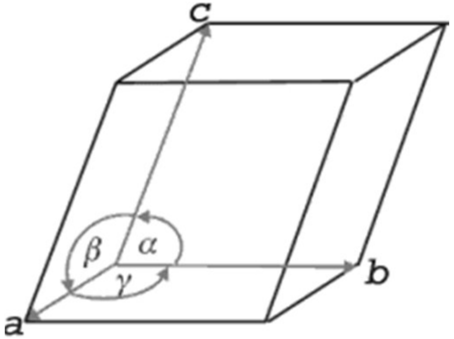
Single Crystal: Composed of only one particular type of space lattice.

Polycrystalline matter: Clusters of multiple crystals.

7.1.3 Crystal systems and Bravais Lattices

a. Crystal systems

There are a total of seven types of crystal systems differing in symmetry.



Crystal systems	Characteristic symmetry elements	Unit cell parameters	Choice of axis	Lattic Point Group
Triclinic	Nil	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$		C_i
Monoclinic	C_2, σ_h	$a \neq b \neq c$ $\alpha = \gamma = 90° \neq \beta$	b // C_2	C_{2h}
Orthorhombic	$3C_2$, $2\ \sigma_h$	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$	a, b, c // $3C_2$	D_{2h}

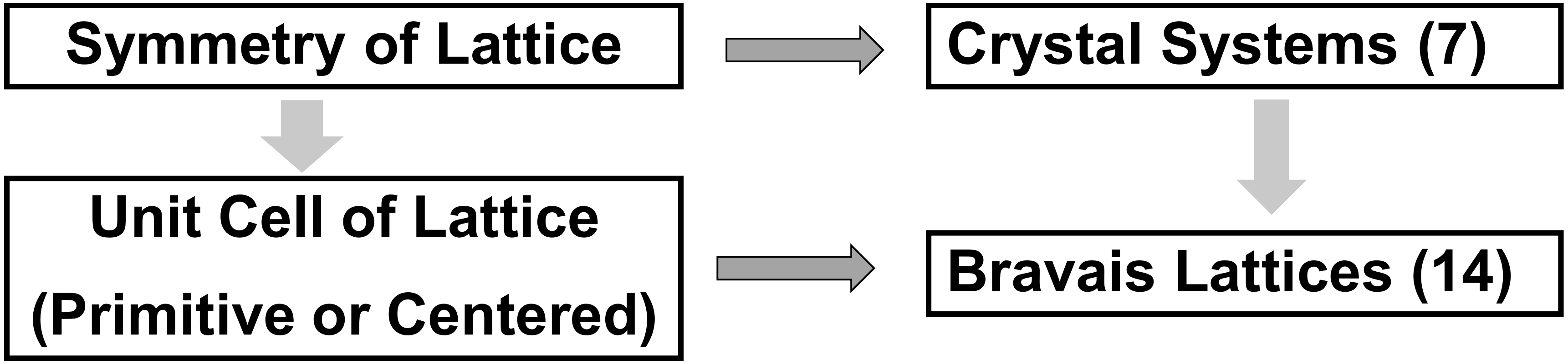
Unit cell is chosen in such a way that it contains as many symmetry elements of the lattice as possible and has the smallest volume.

Trigonal	C_3	Rhombohedral $a=b=c$, $\alpha=\beta=\gamma<120^\circ\neq 90^\circ$		D_{3d}
		Hexagonal $a=b\neq c$, $\alpha=\beta=90^\circ$ $\gamma=120^\circ$		D_{6h}
Tetragonal	C_4	$a=b\neq c$, $\alpha=\beta=\gamma=90^\circ$	c // C_4	D_{4h}
Hexagonal	C_6	$a=b\neq c$ $\alpha=\beta=90^\circ$, $\gamma=120^\circ$	c // C_6	D_{6h}
Cubic	$4C_3$	$a=b=c$ $\alpha=\beta=\gamma=90^\circ$	Four C_3 axes are parallel to the body diagonals of the cube	O_h

b. Bravais Lattices: (14) [developed by Bravais in 1850 !]

Primitive cell: minimal size，one lattice point only!

Unit Cell of Bravais Lattice: having the highest symmetry & minimal size, may contain more than one lattice point.



Symmetry of Lattice → **Crystal Systems (7)**

Unit Cell of Lattice (Primitive or Centered) → **Bravais Lattices (14)**

Triclinic	Monoclinic	Orthor-hombic	Tetragonal	Cubic	Trigonal	Hexagonal
aP	mP, mC	oP, oC oF, oI	tP, tI	cP, cI, cF	hR, hP	hP

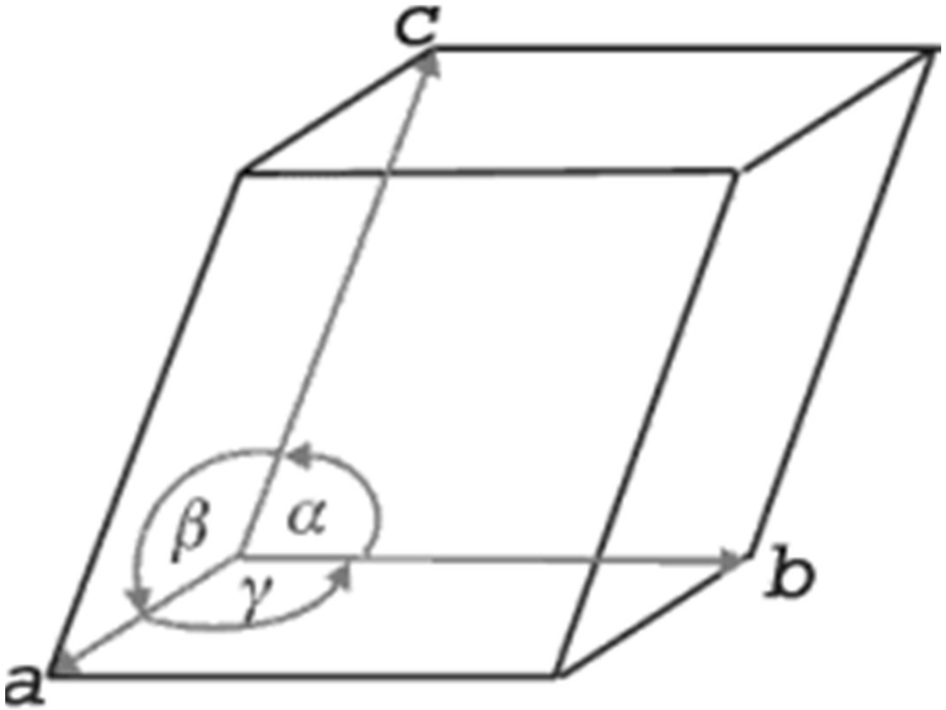
Lowercase letter (crystal system) + Capital letter (Type of cell)

e.g., hR-- R-centred hexagonal, mC-- C-centred monoclinic

* Triclinic

$a \neq b \neq c$

$\alpha \neq \beta \neq \gamma$



aP (Primitive)

- **Triclinic crystal system has the lowest symmetry.**
- **It can be simply represented by a primitive cell.**
- **Symmetry element: *i***

* Monoclinic

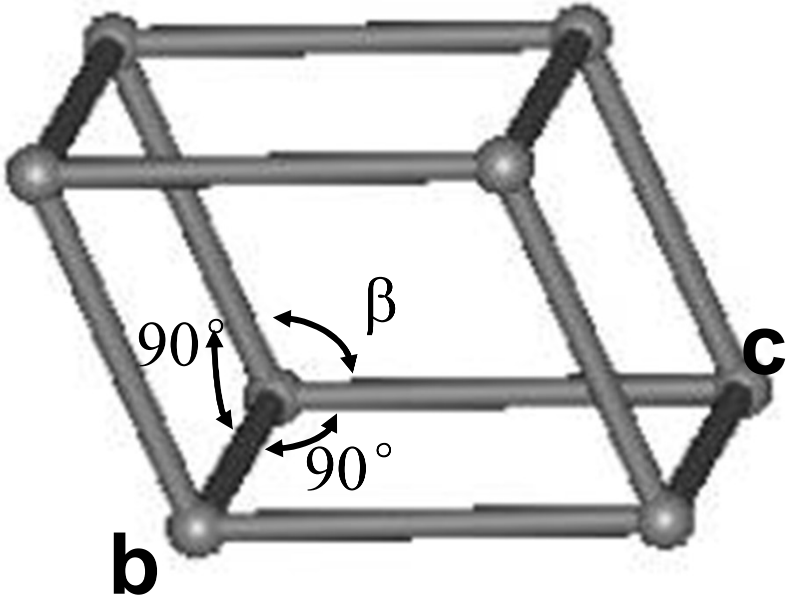
A primitive cell contains one lattice point and a C-centered unit cell contains two lattice points.

a≠b≠c

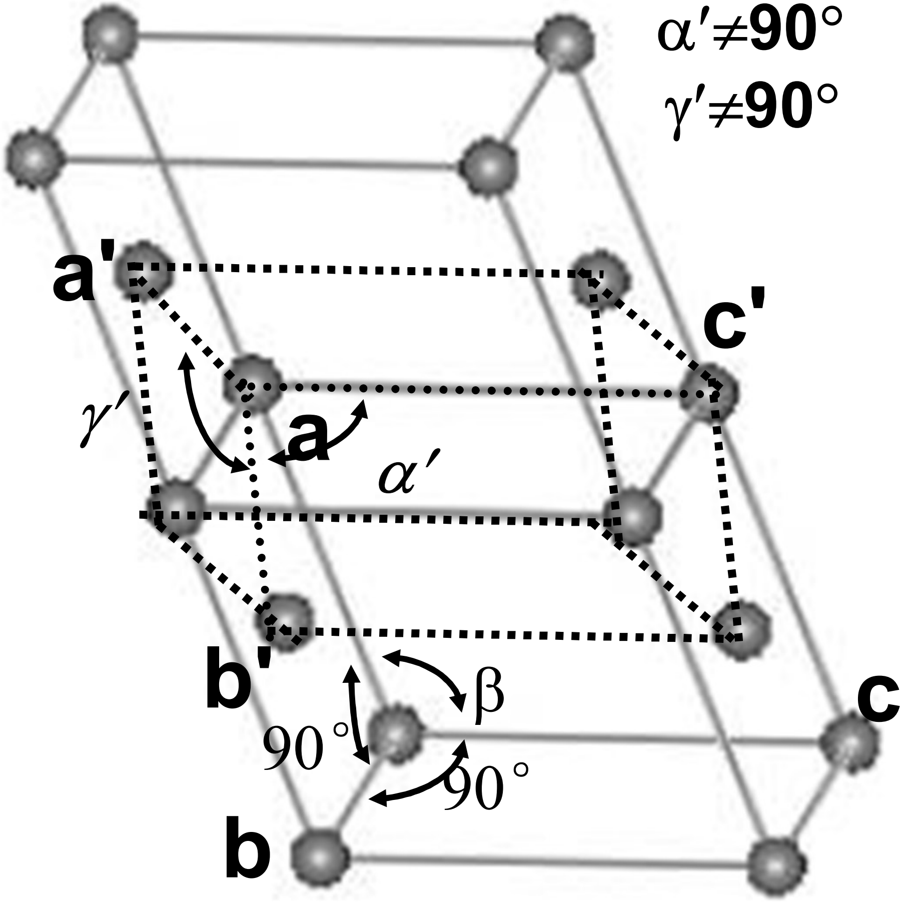
$\alpha = \gamma = 90^{o} \neq \beta$

Sym. Elements:

i, C_2(//b), σ_h,



mP (Primitive)



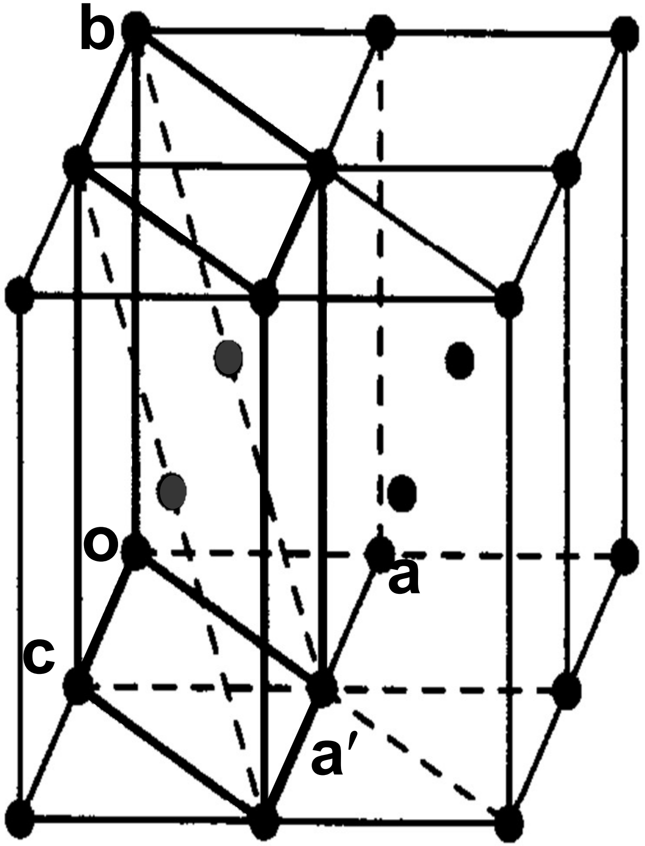
$\alpha' \neq 90°$

$\gamma' \neq 90°$

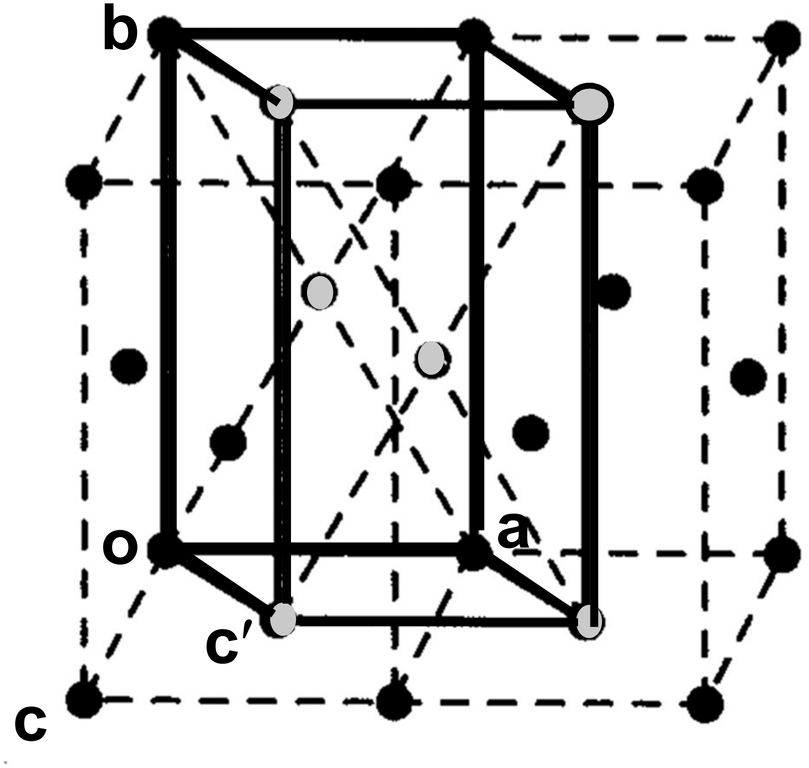
mC (C-centered or A-centered)

The primitive cell of a C-or A-centered monoclinic is triclinic!

Does I- or F-centered monoclinic lattice exist?



mI ? = mC



mF ? = mC

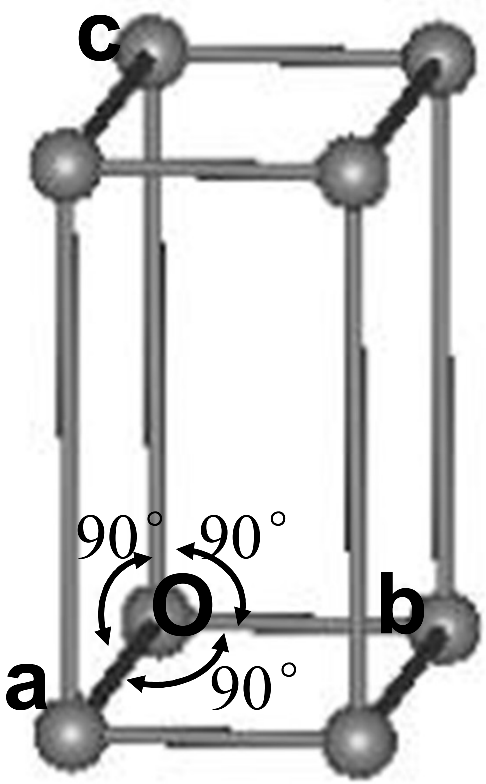
Both I- and F-centered monoclinic are unnecessary and can be represented by a mC!

*** Orthorhombic**

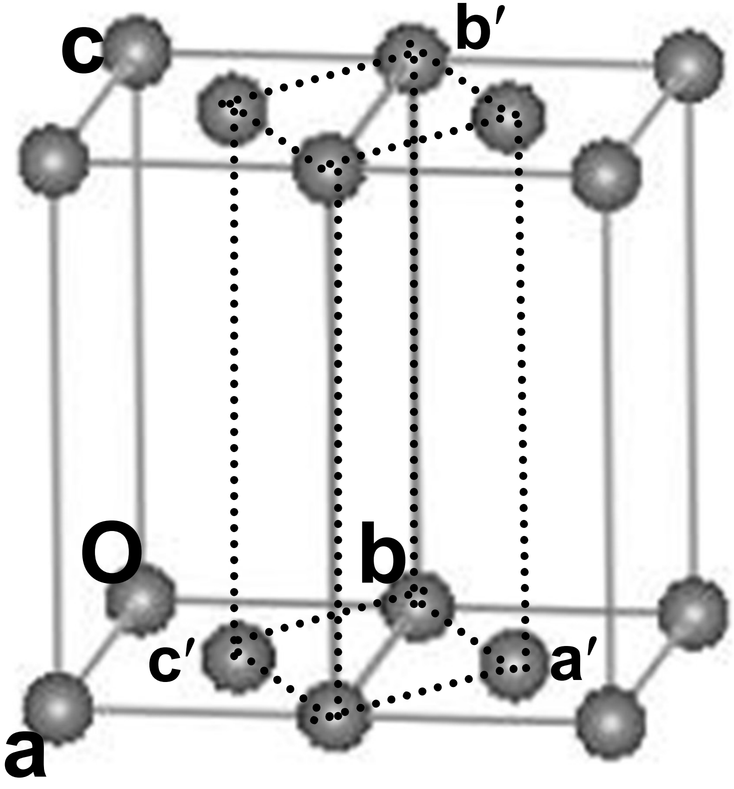
$\mathbf{a \neq b \neq c}$

$\alpha = \beta = \gamma = \mathbf{90^o}$

- The primitive cell of a C-centred orthorhombic lattice is actually monoclinic!



oP (Primitive)



C-centered or A-centered or B-centered

* Orthorhombic

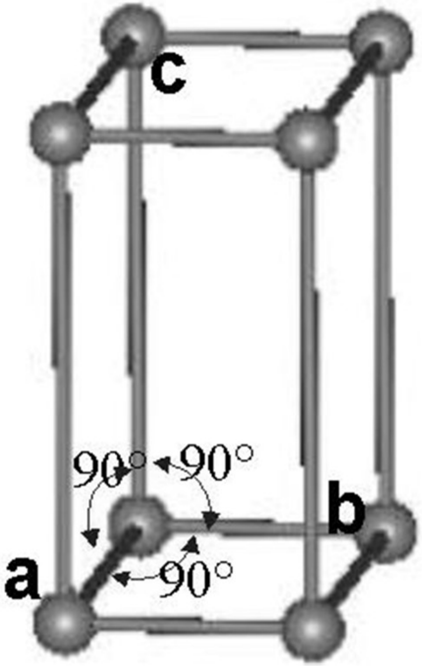
$a \neq b \neq c$

$\alpha = \beta = \gamma = 90^{o}$

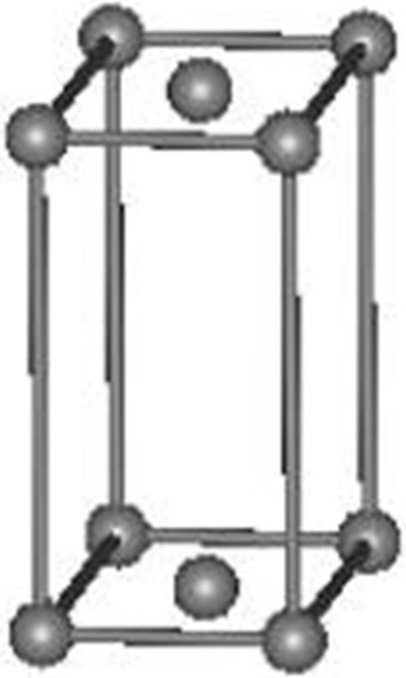
→

Sym. Elements:

$3C_2$ (//a,b,c), *i*, $3\sigma_h$ (//A,B,C)

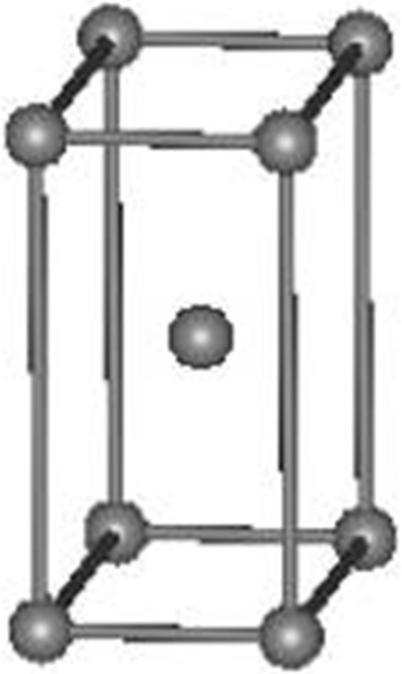


oP



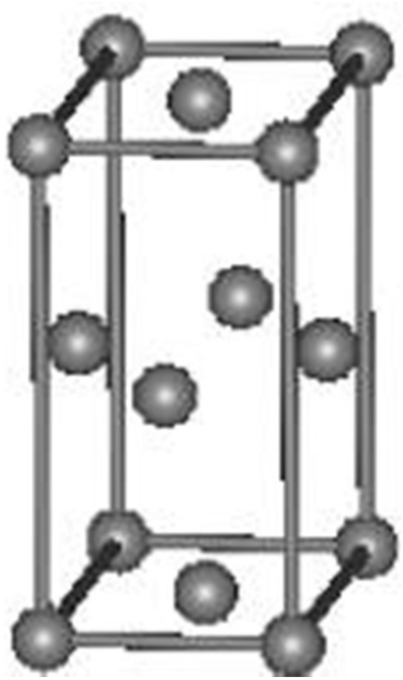
oC

or oA or oB



oI

(In-centered)

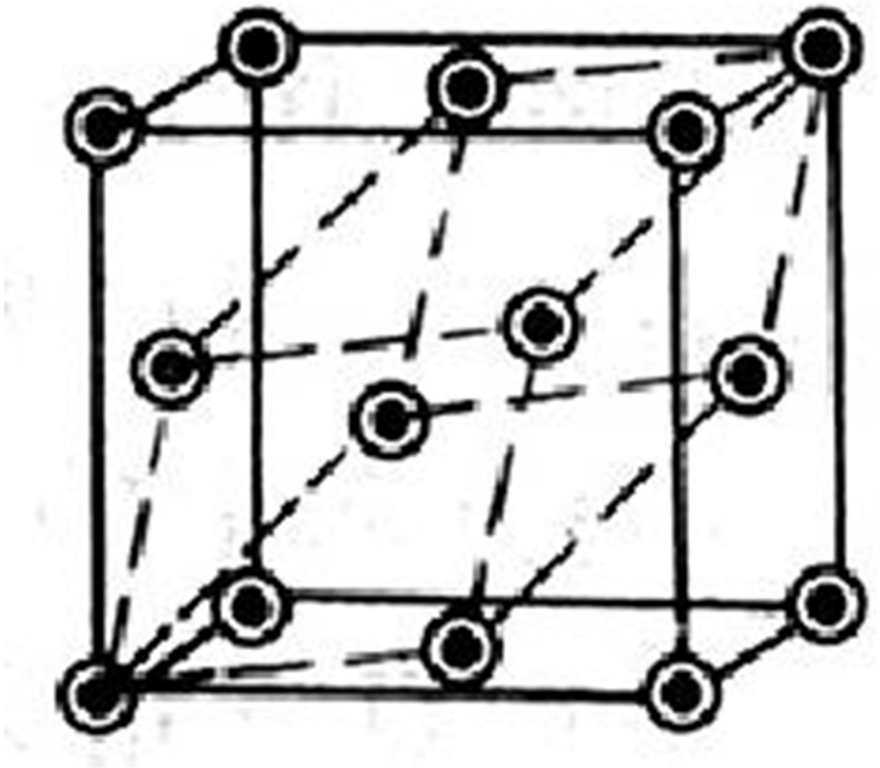


oF

(Face-centered)

* Orthorhombic

Face-centered cell (**oF**) and its primitive cell



- **A Face-centered unit cell contains four lattice points!!**
- Its primitive cell is triclinic, and does not contain such symmetry elements as C_2 and σ_h of the lattice.

Question: For a body-centered orthorhombic lattice, is its primitive cell triclinic or monoclinic?

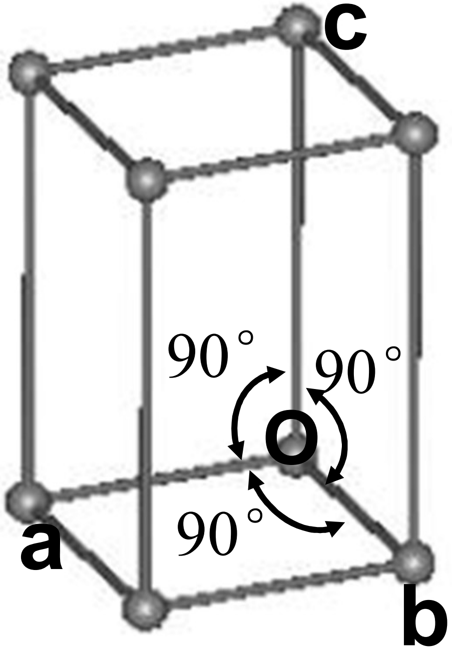
* Tetragonal

$a=b\neq c$

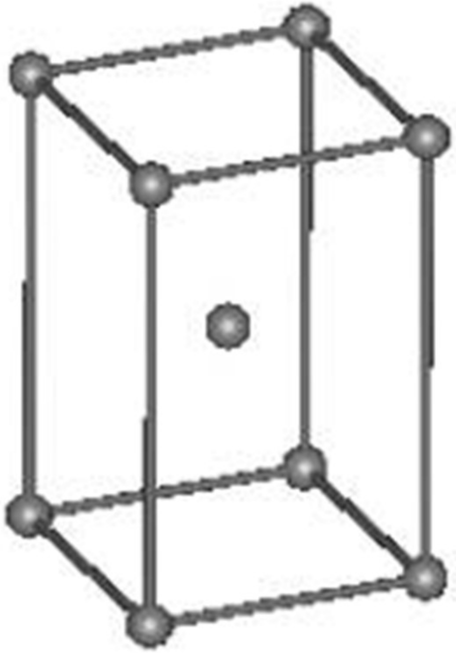
$\alpha=\beta=\gamma=90^{o}$

Sym. Elements:

C_4(//c), $2C_2$ (//a,b), *i*, $3\sigma_h$ ($\perp$a,b,c)

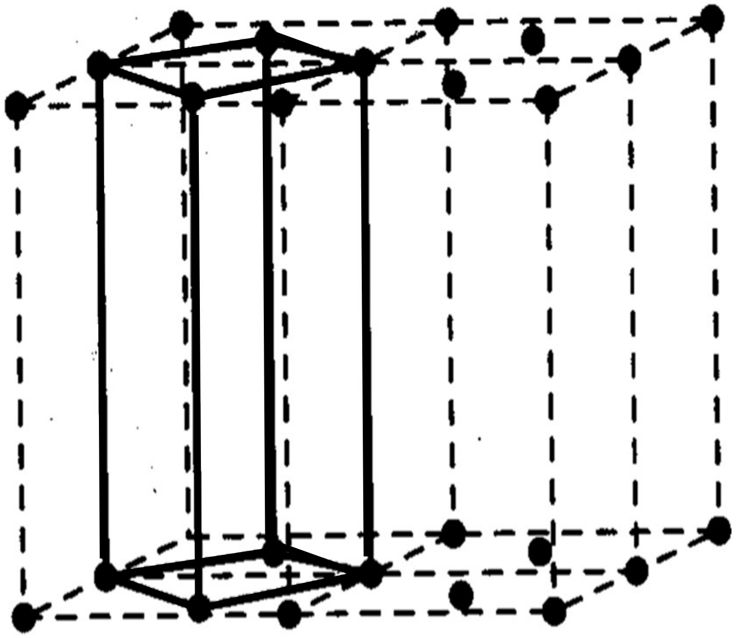


tP

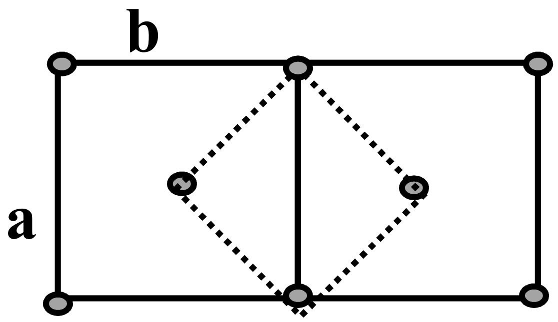


tI

Does a C- or F-centered tetragonal lattice exist?



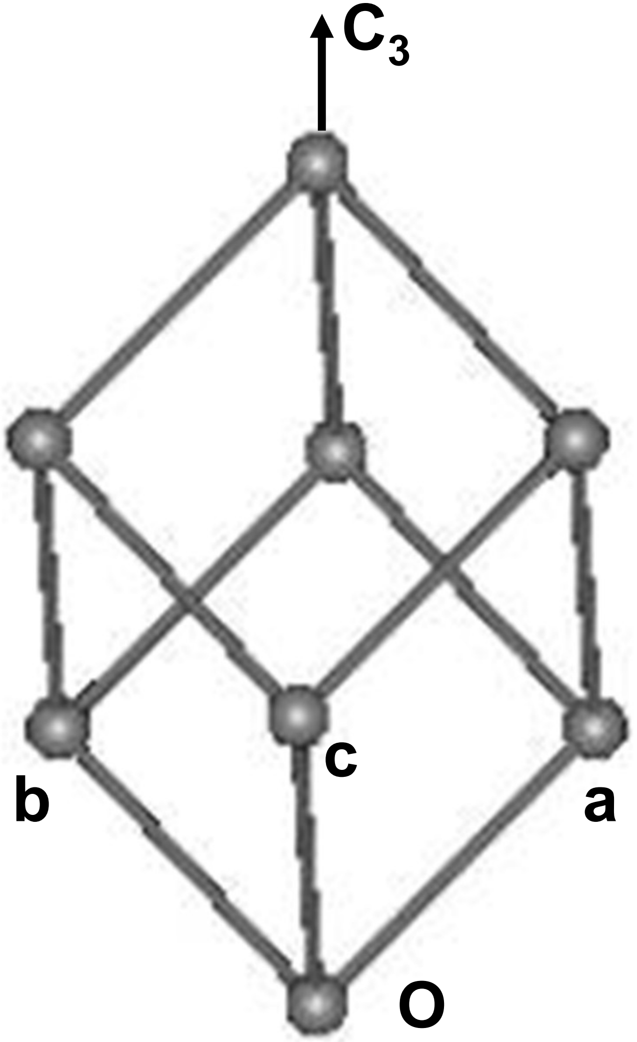
tC = tP



- **Neither C-centered tetragonal nor F-centered tetragonal exists.**

Please prove it!

* Trigonal ---- Rhombohedral



a=b=c

$\alpha = \beta = \gamma \neq 90^{\circ}$

Sym. Elements: C_3, *i*,

hR

A rhombohedral lattice can be represented by a R-centered hexagonal lattice!

* Hexagonal

$a=b\neq c$

$\alpha=\beta=90^o$,

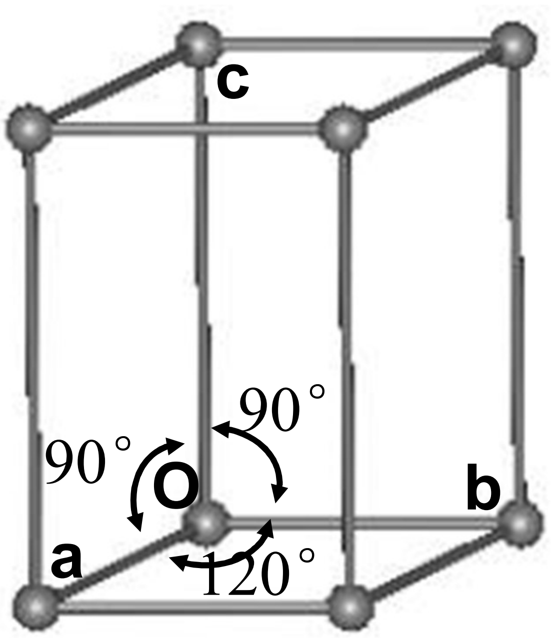
$\gamma=120^o$

Sym. Elements:

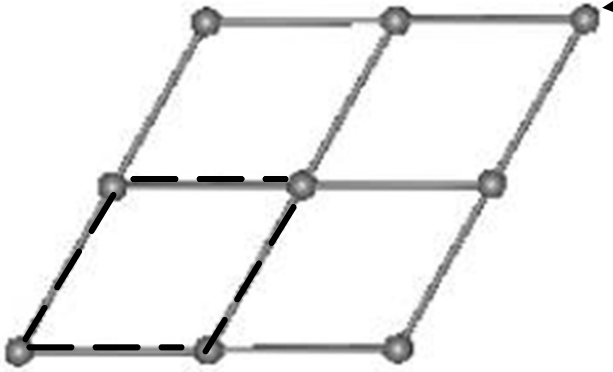
C_6(//c), *i*,

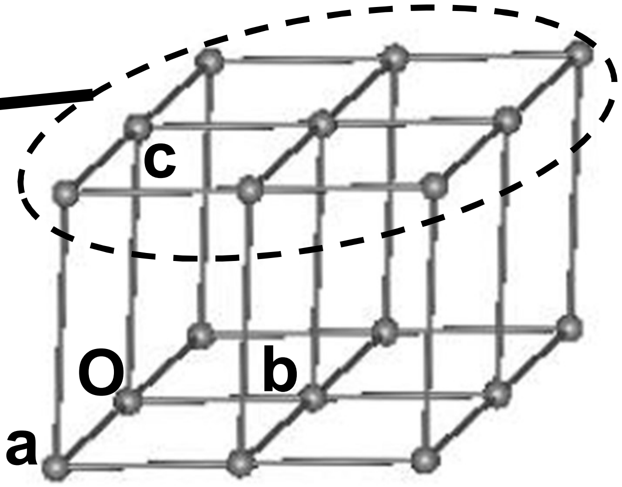
σ_h (⊥c, //C)

hP unit cell

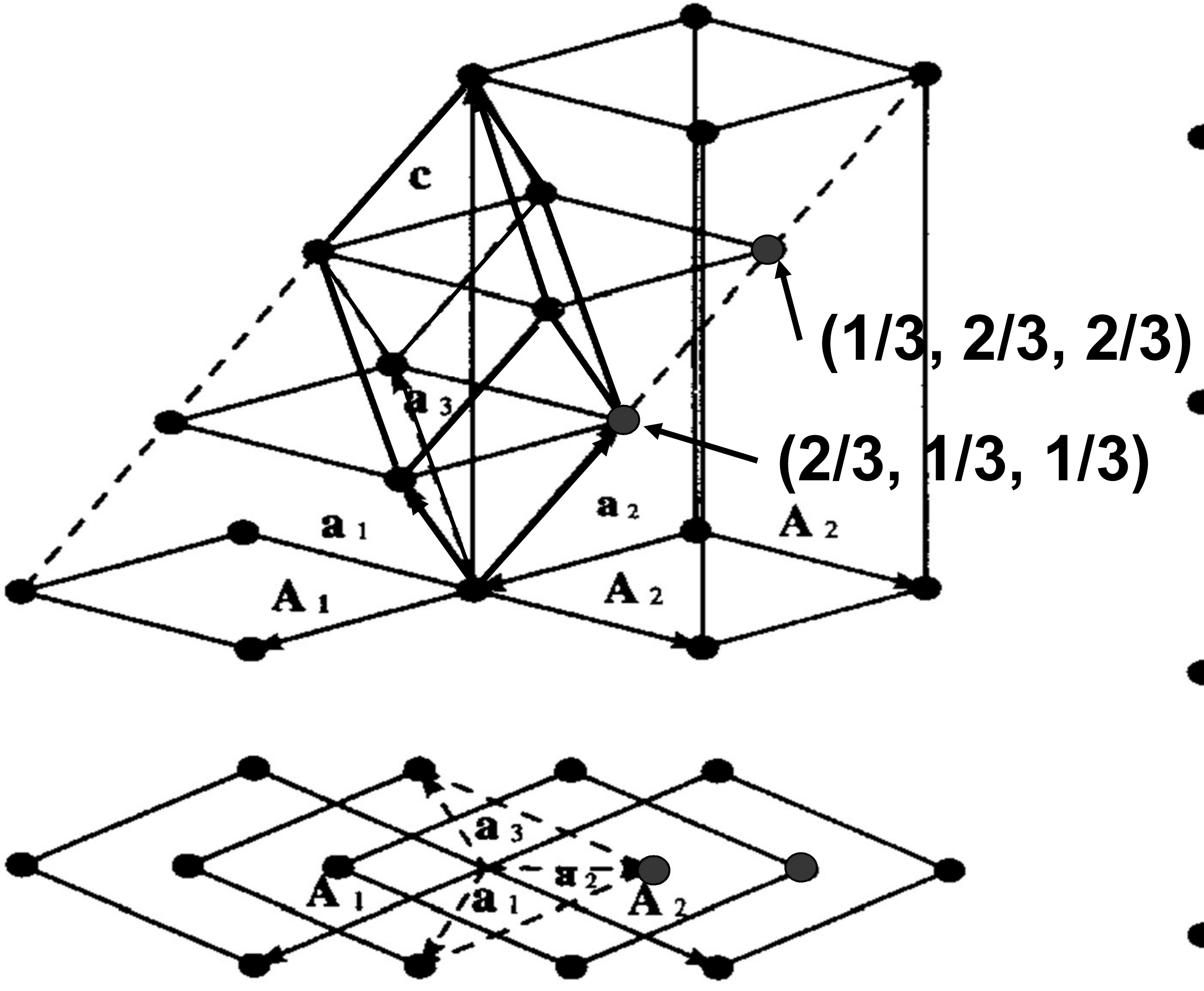


Hexagonal 2D lattice





a. Primitive rhomohedral = r-centered hexagonal

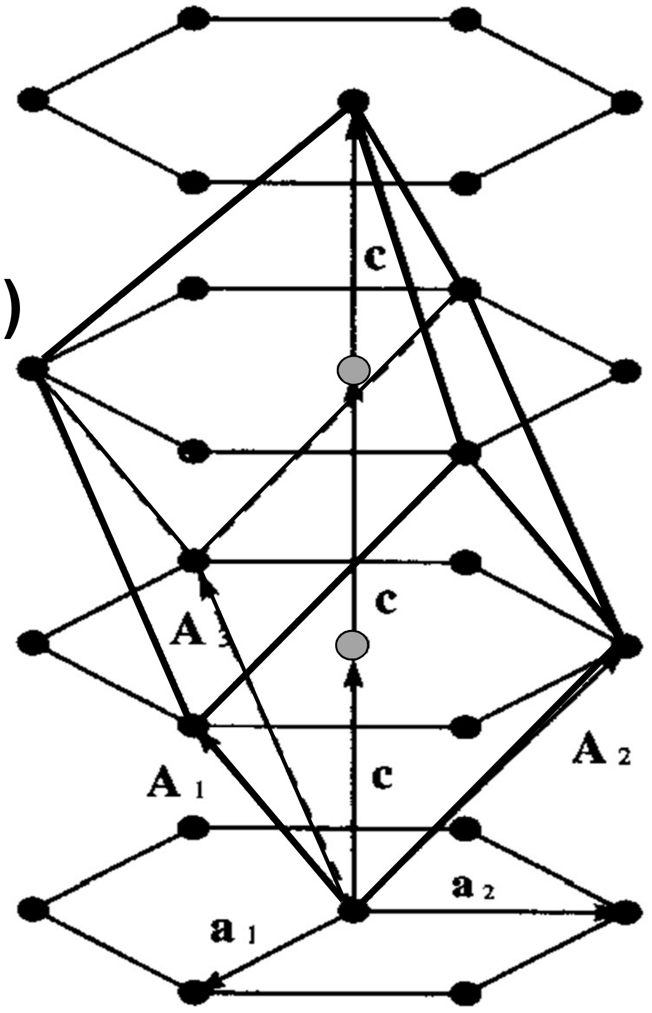


(1/3, 2/3, 2/3)

(2/3, 1/3, 1/3)

(a)

b. primitive hexagonal r-centered rhombohedral



(b)

*** Cubic**

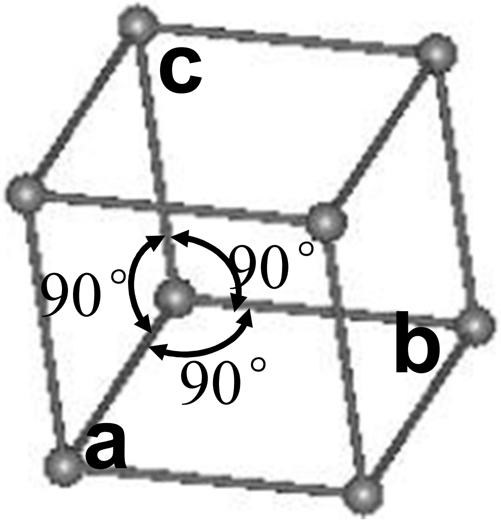
$a=b=c$

$\alpha = \beta = \gamma = 90^{o}$

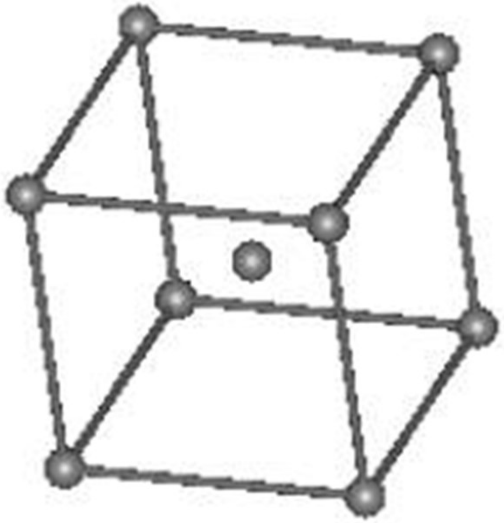
Sym. Elements:

$3C_4$(//a,b,c), $4C_3$, *i*,

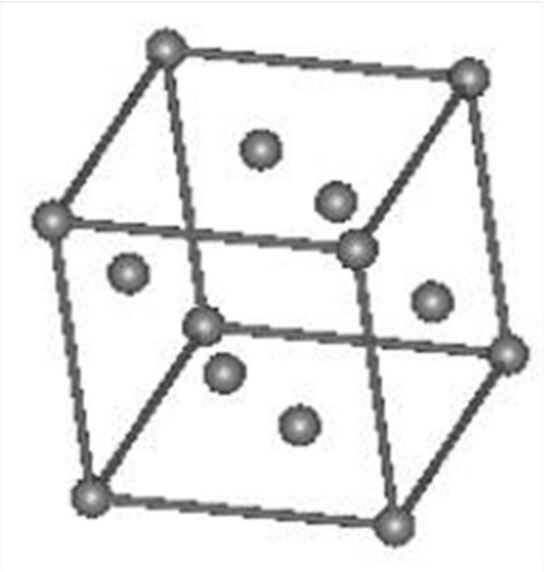
$3\sigma_h$ ($\perp$a,b,c, //A,B,C)



cP



cI

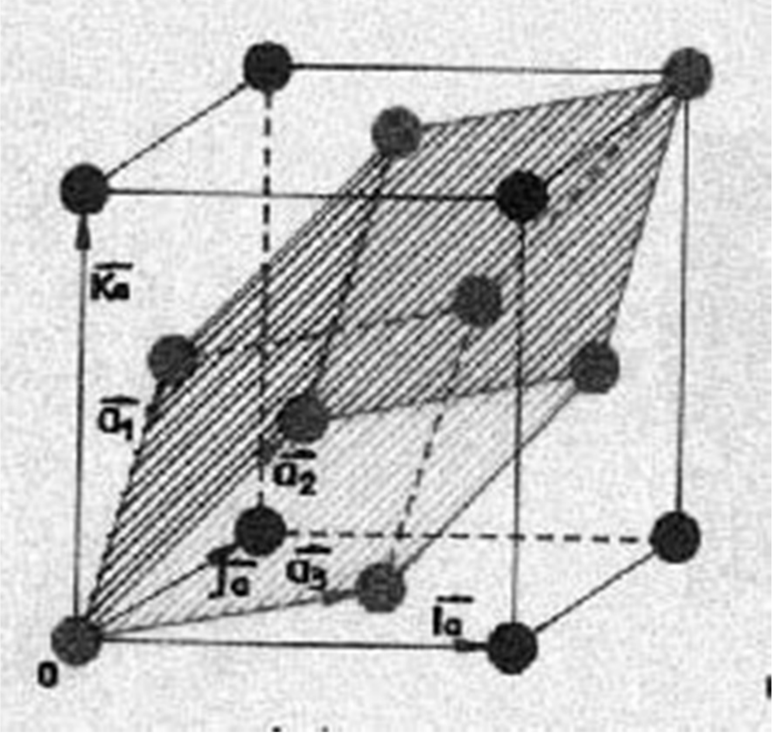


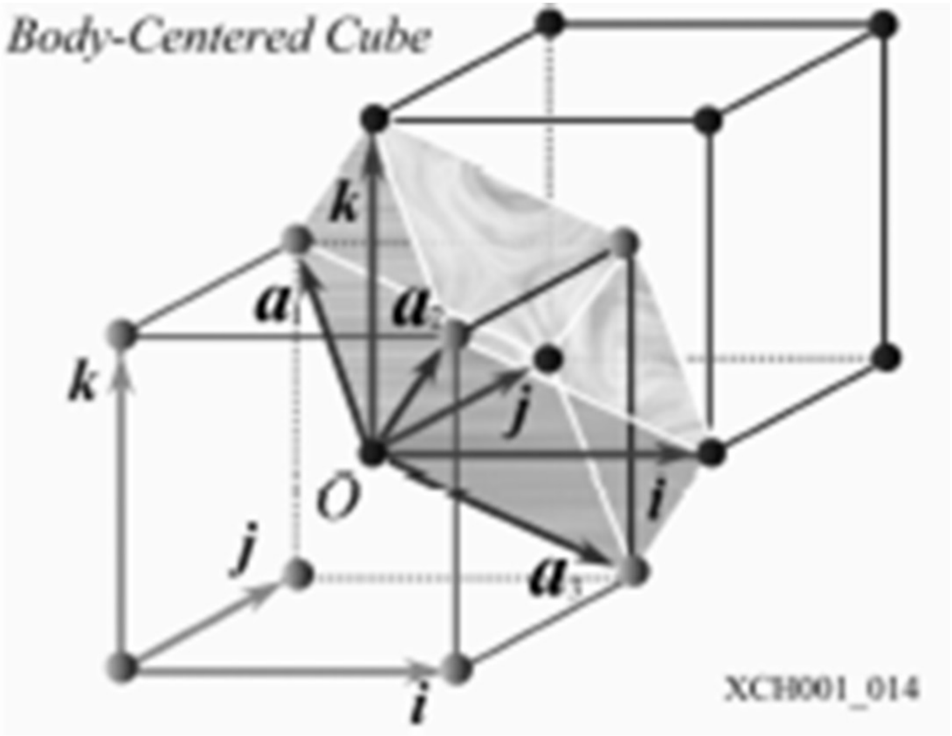
cF

Is there a c-centered cubic lattice?

- Introducing a C-center eliminates all C_3-axes and results in only one C_4 axis. The lattice should be actually tetragonal.

- The primitive cell of a **fcc** or ***bcc*** lattice is rhombohedral, which does not include the $\boldsymbol{C_4}$–axes of the lattice!





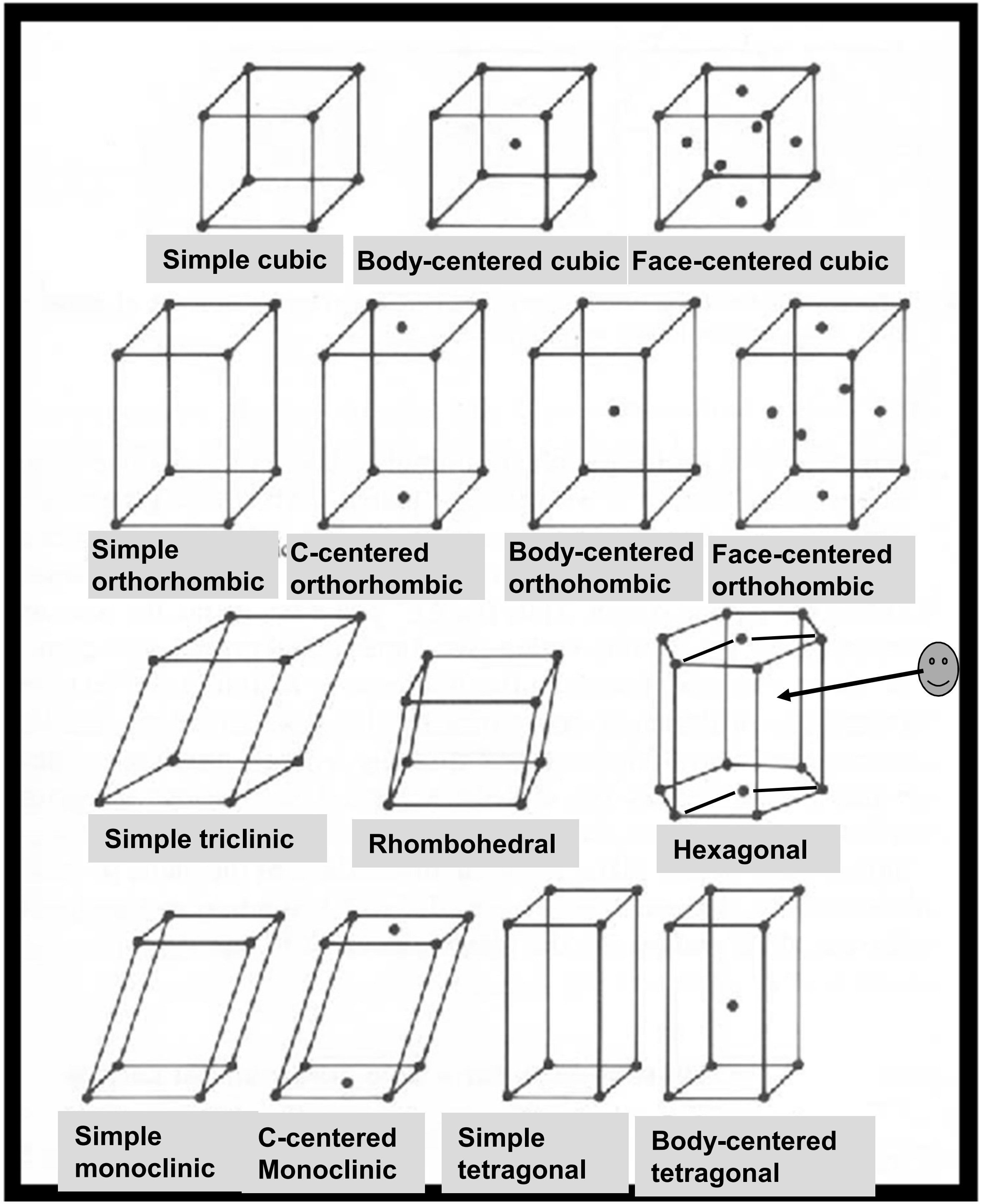
Bravais Lattices: (14)

Unit Cell: the highest symmetry + minimal size

Centered unit cell is thus introduced to contain the highest symmetry of the lattice.

Crystal systems	P	C	I	F
Triclinic				
Monoclinic				

Orthorhombic				
Trigonal				
Tetragonal				
Hexagonal				
Cubic				



Augusta Bravais

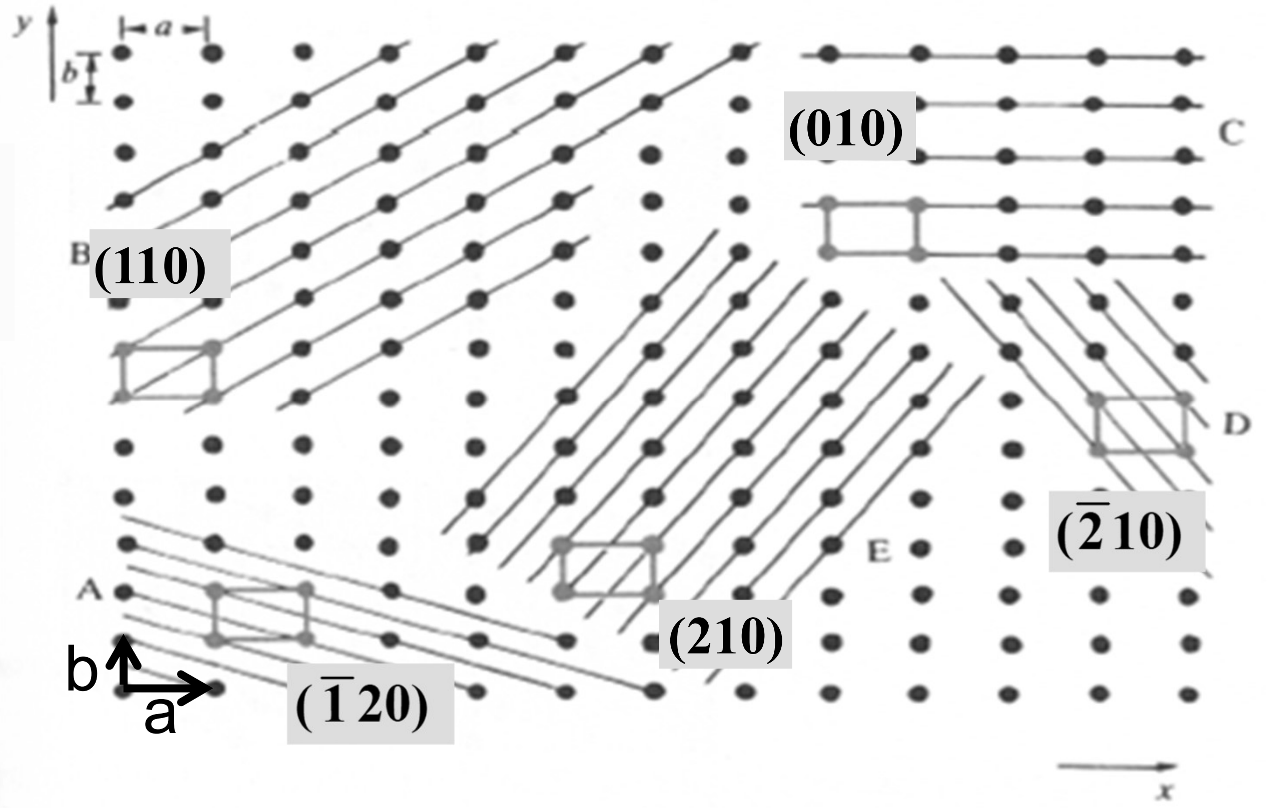
Died on 30 Mar 1863 (born 23 Aug 1811) French physicist best remembered for his work on the lattice theory of crystals; Bravais lattices are named for him.

7.1.4 Crystal Planes and Miller Indices

a. Lattice planes

A 2D lattice plane, i.e. (001), of an oP lattice.

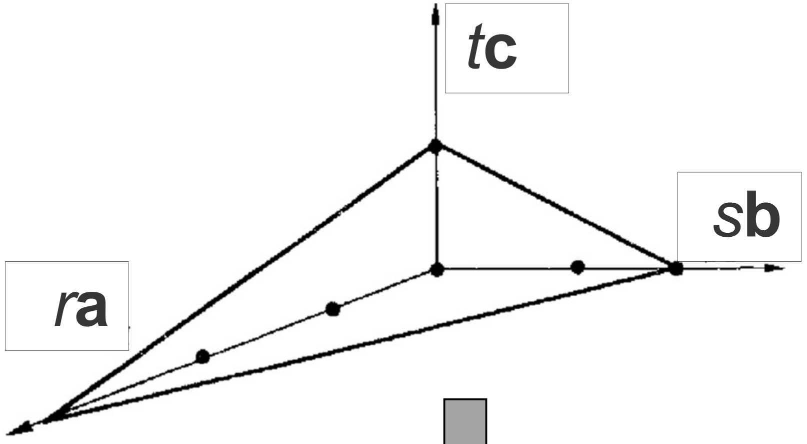
Those lines are the projections of crystal planes (//c-axis) onto this plane.



- **It is possible to describe certain directions and planes with respect to the crystal lattice using a set of three integers referred to as Miller Indices.**
- **Miller indices describe the orientation and spacing of a family of planes.**

b. Miller indices (hkl)

- **Introduced in 1939 by the British mineralogist W. H. Miller.**
- **Miller indices are the reciprocal intercepts of the lattice plane on the unit cell axes.**



$$\frac{1}{r}:\frac{1}{s}:\frac{1}{t}=h:k:l$$

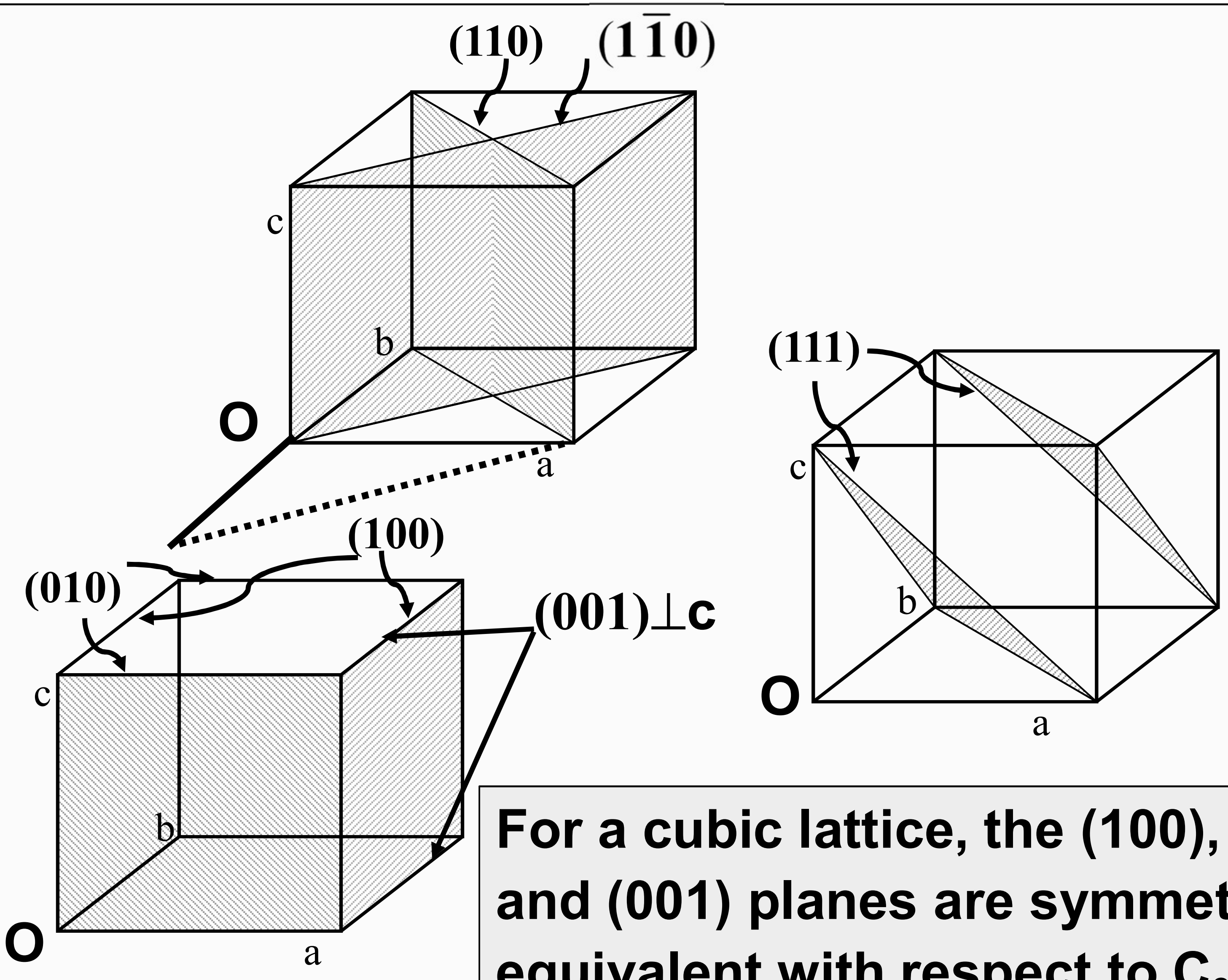
For this special case**:** ***r* = 3, *s* = 2, *t* = 1**

***h*:*k*:*l* = (1/3):(1/2):(1/1) = 2:3:6**

→ The Miller index of this lattice plane is (236)!

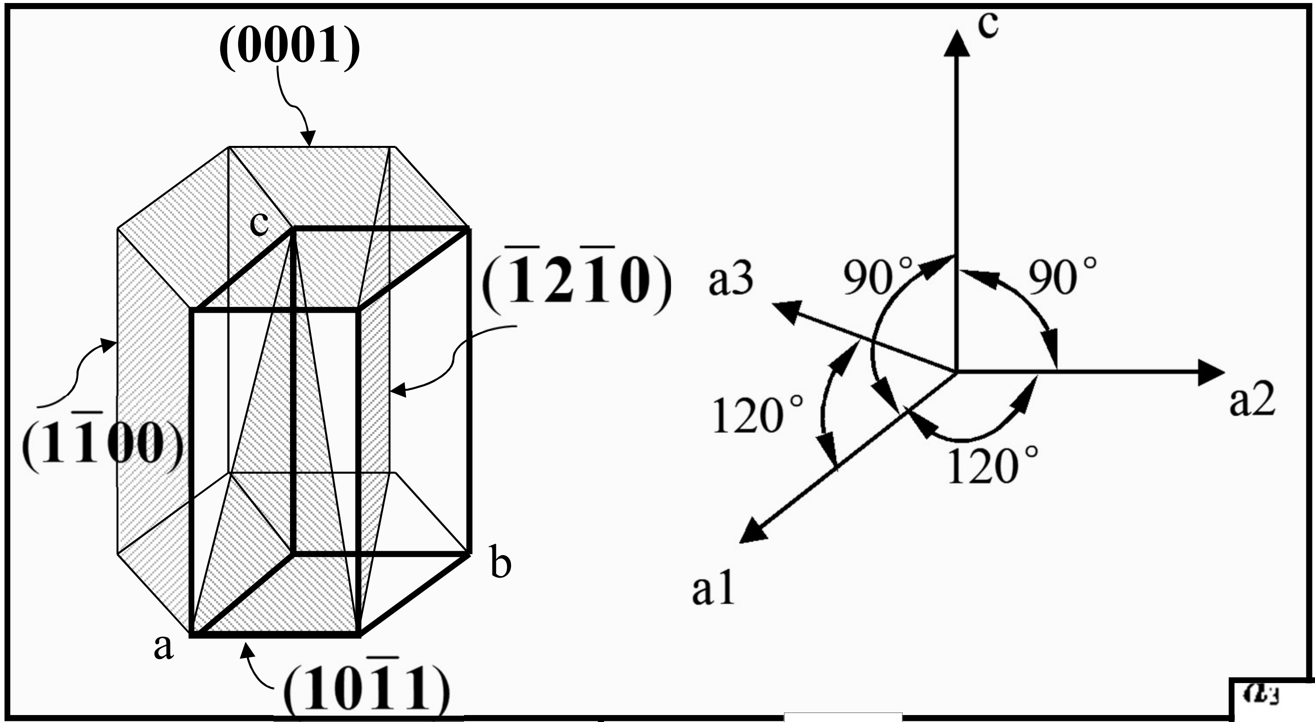
Question: why do we not use ***r:s:t*** directly to represent a lattice plane?

Example: Miller indices in a cubic lattice



For a cubic lattice, the (100), (010), and (001) planes are symmetry-equivalent with respect to C_3 axes.

Hexagonal, using four axes (a1,a2,a3,c)

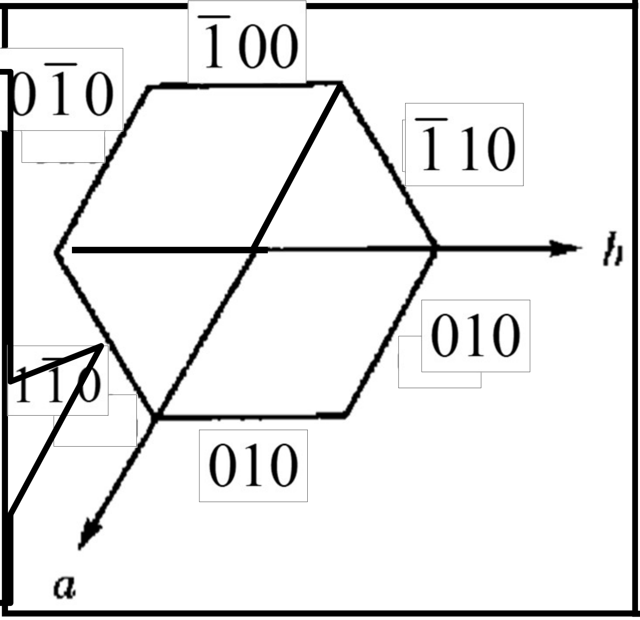


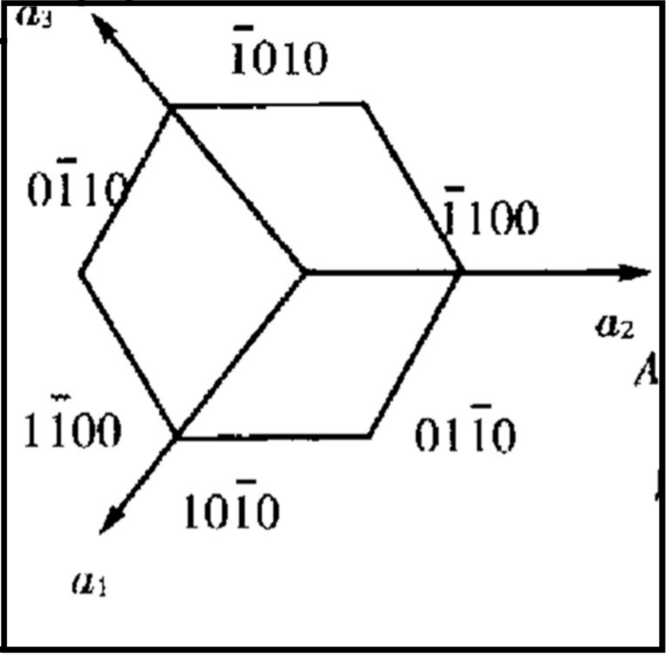
(hkil), i = -(h+k)

A third axis:

$\mathbf{a_3 = -(a_1 + a_2)}$

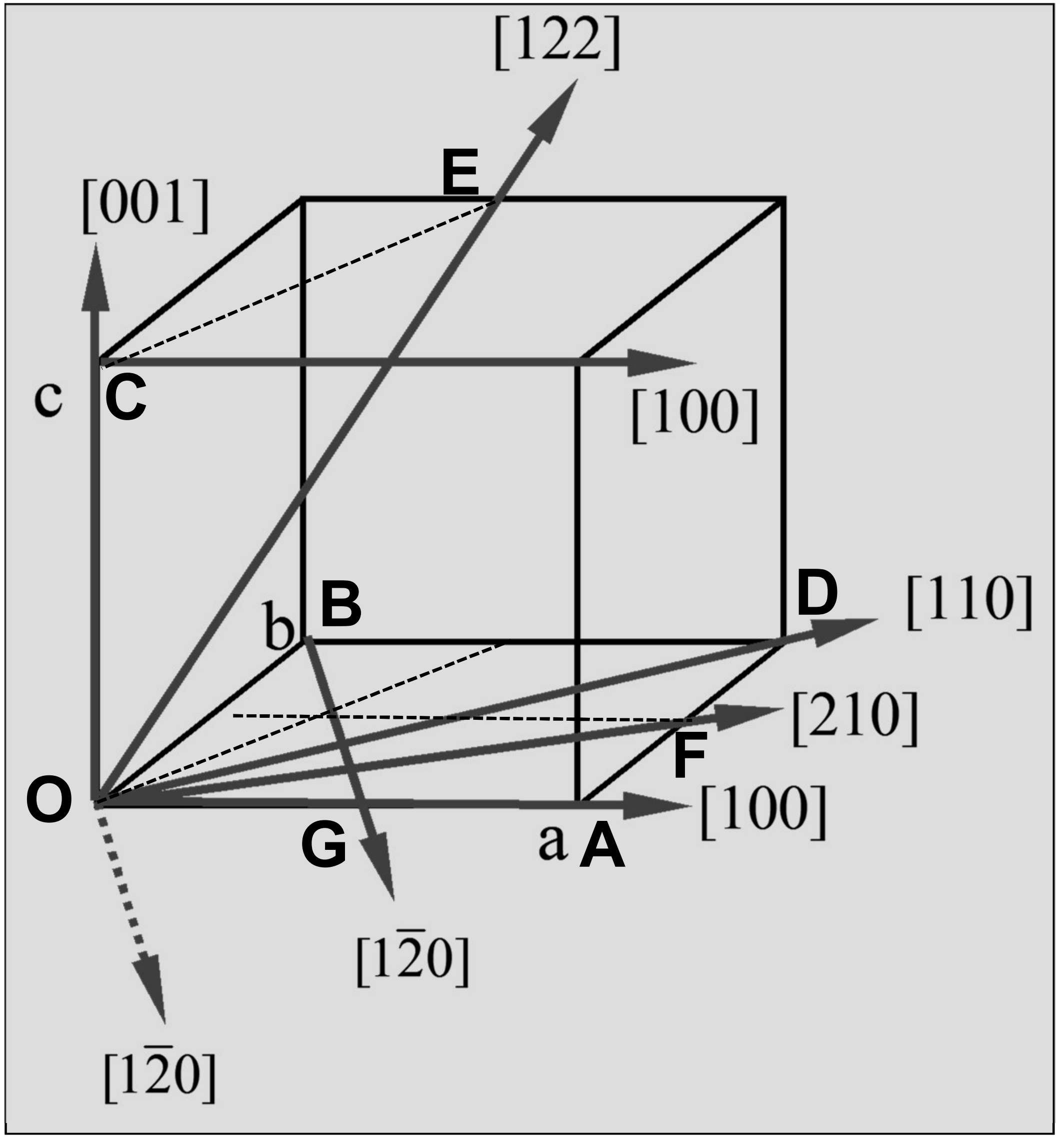
The use of only two basis vectors a & b does not reflect the C_6- symmetry among such planes as (100), $(1\bar{1}0)$ … !





C. Directions in lattice

Miller Indices [uvw]



- *The direction of a lattice vector, **ua + vb +wc**, is* represented by three indices **[uvw]***, which are* prime to each other*.*

e.g. ***a*** axis: **[100]. (OA)**

b axis: **[010]. (OB)**

c axis: **[001]. (OC)**

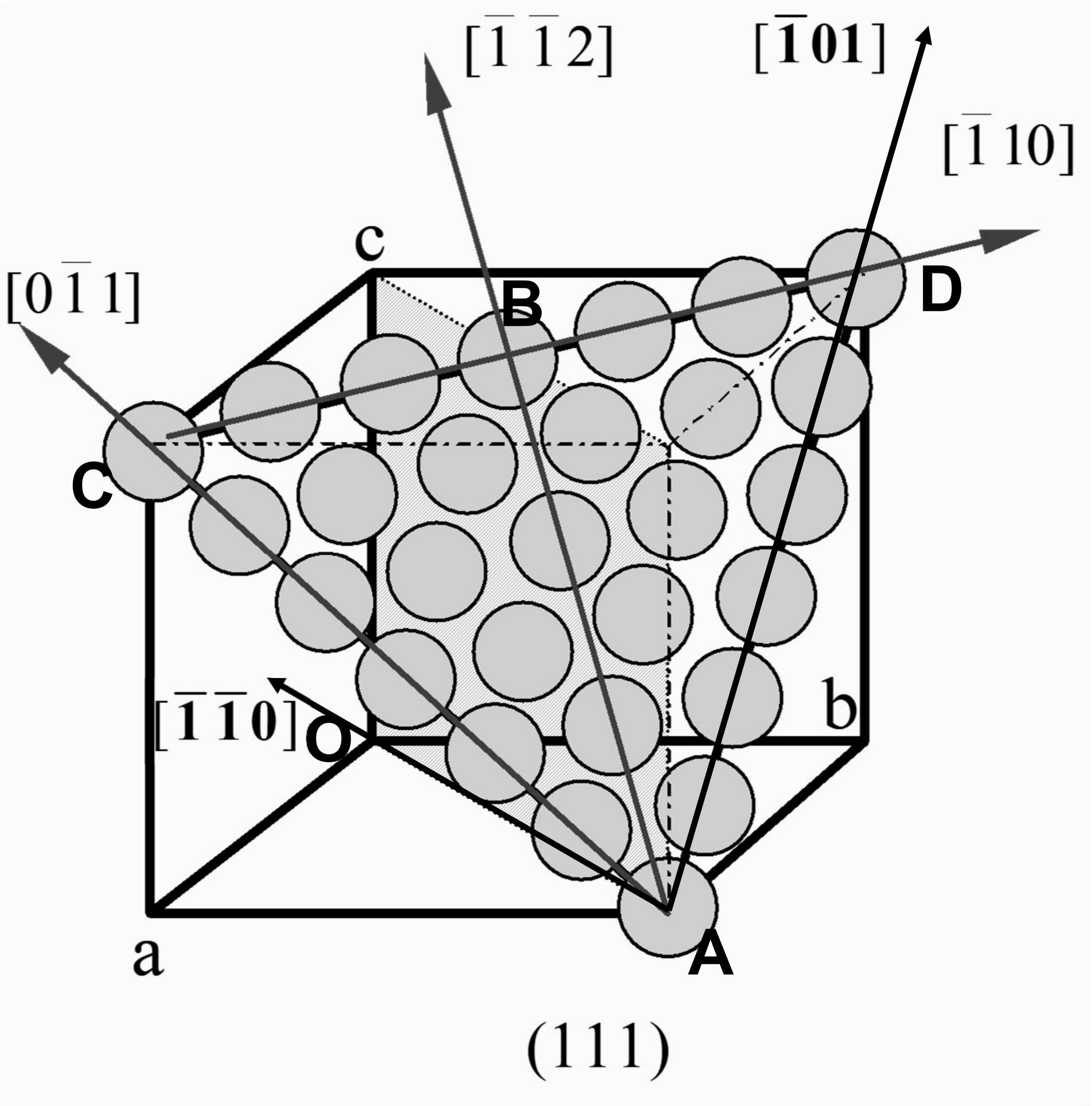
OD = ***a* + *b*** → **[110]**.

OE = ***0.5a* + *b* + *c*** → **[122]**

OF = ***a* + *0.5b*** → **[210]**

BG = ***0.5a* - *b*** → **[210]**

Example: Directions on the (111) plane of a cubic lattice.

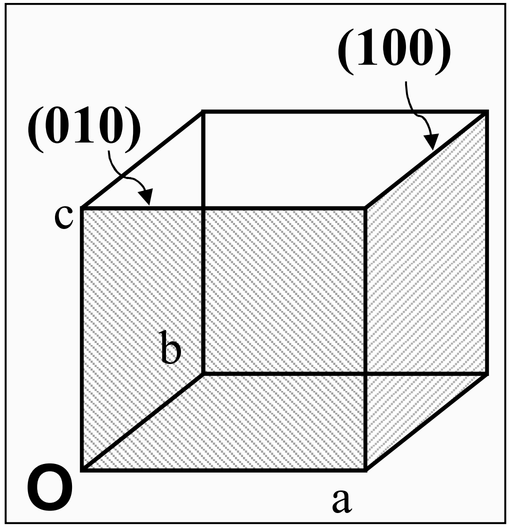


A (1.0, 1.0, 0.0); B(0.5, 0.5, 1.0);
C(1.0, 0.0, 1.0); D(0.0, 1.0, 1.0)

- Various lattice vectors can be defined by the lattice points within the (111) plane.
- e.g., the vector from points A to B, i.e., -0.5a - 0.5b + c, defines the direction $[\bar{1}\bar{1}2]$.
- The vector from points A to C, -b+c, is defines the direction $[0\bar{1}1]$.
- The vector CD, i.e., -a+b, defines the direction $[\bar{1}10]$.

Miller indices (hkl) are used to specify the orientation and spacing of a family of planes.

{hkl} are used to specify all symmetry-equivalent sets of planes



e.g., For a cubic lattice system, the lattice planes (100), (010), (001) are symmetry-equivalent upon C_3 or C_4 rotations, and can be represented by {100}.

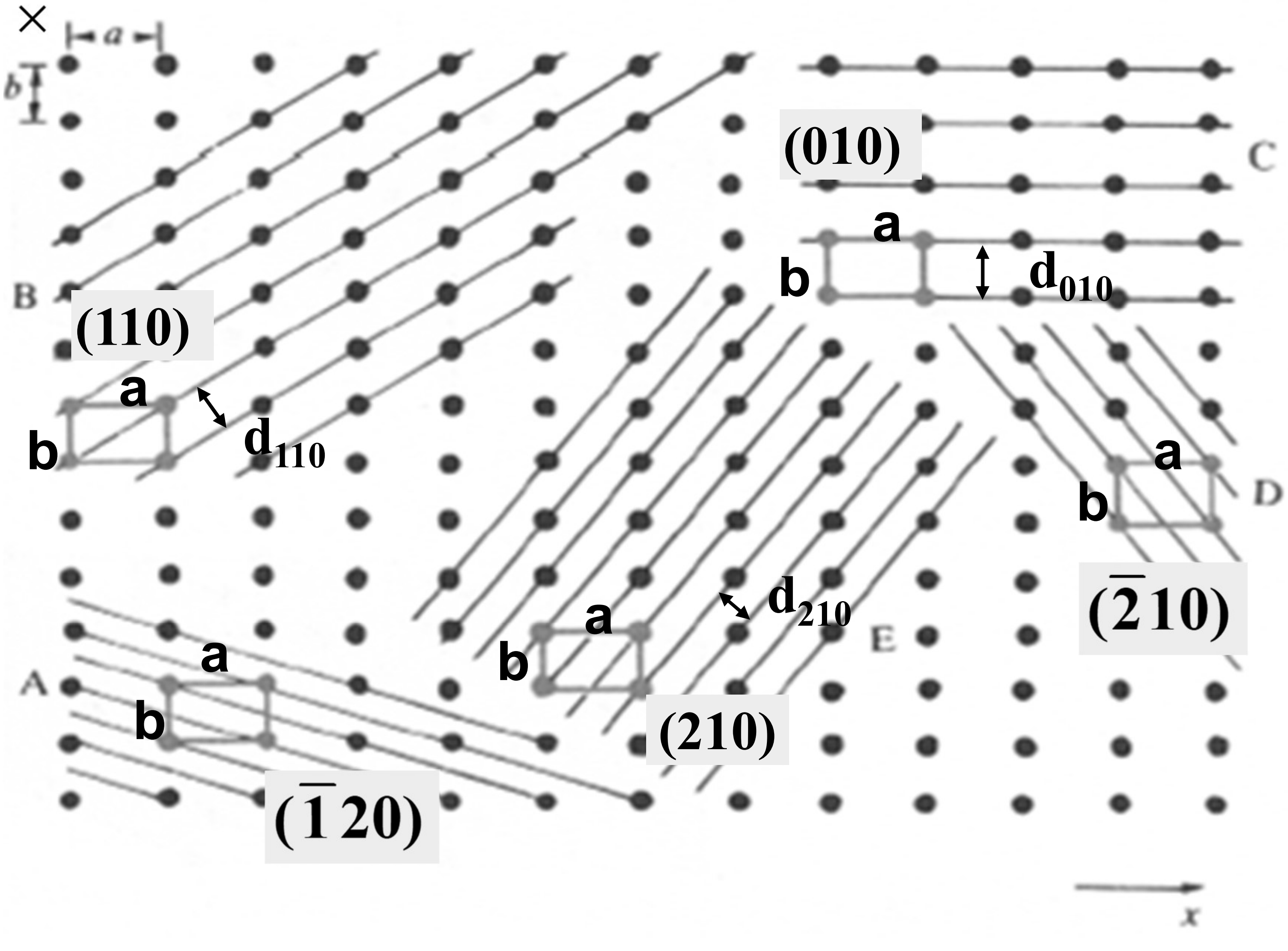
[uvw] zone axis **Direction Vector = u*a* + v*b* + w*c***

Miller indices: [hkl] are used to specify a direction in space with respect of the unit cell axes.

<hkl> are used to specify a set of symmetry-equivalent directions.

d. d-spacing d_{hkl}

The spacing between adjacent planes in a family is referred to as a "d-spacing".



oP:

Projections of crystals planes (//c-axis) on the (001) plane.

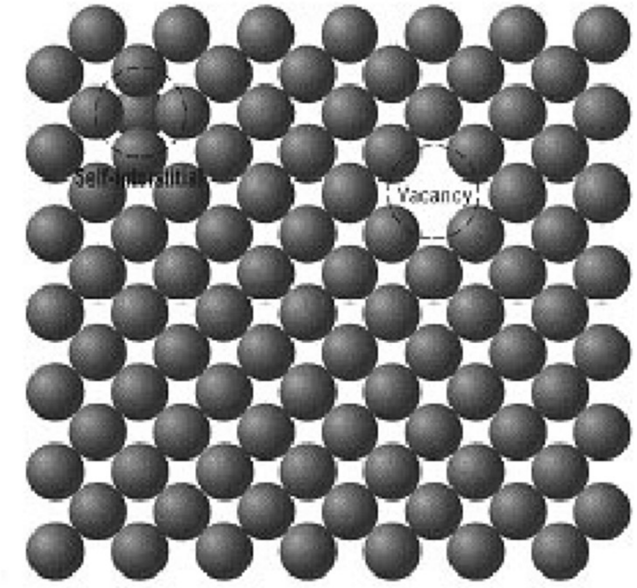
The spacing between adjacent planes in a family is referred to as a “d-spacing”

- **Cubic :** $1/d^2 = (h^2+k^2+l^2)/a^2$ or $d^2 = a^2/(h^2+k^2+l^2)$
- **Tetragonal:** $1/d^2 = (h^2+k^2)/a^2 + l^2/c^2$
- **Orthorhombic:** $1/d^2 = h^2/a^2+k^2/b^2 + l^2/c^2$
- **Hexagonal:** $1/d^2 = (4/3)(h^2+hk+k^2)/a^2 + l^2/c^2$
- **Monoclinic:** $1/d^2 = [(h/a)^2 + (k/b)^2\sin^2\beta + (l/c)^2 - (2hl/ac)\cos\beta]/\sin^2\beta$
- **Triclinic:**

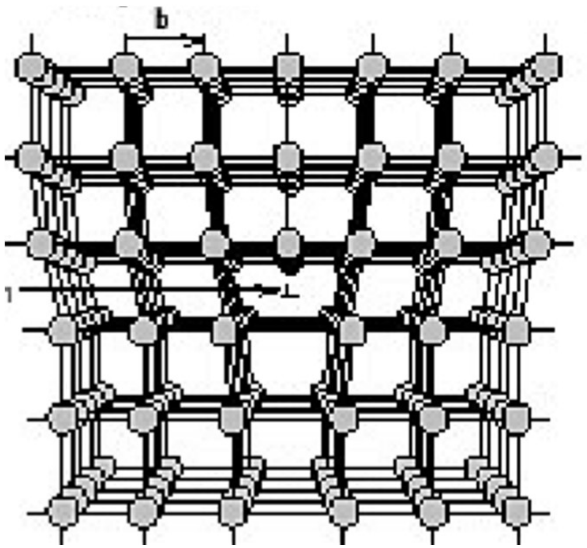
7.1.5 Real crystals and Crystal defects：

Real crystals are only close approximations of space lattices

- **Simplest point defect is a vacancy or vacant lattice site**
- **For most metals:**
- **Caused through thermal vibration**

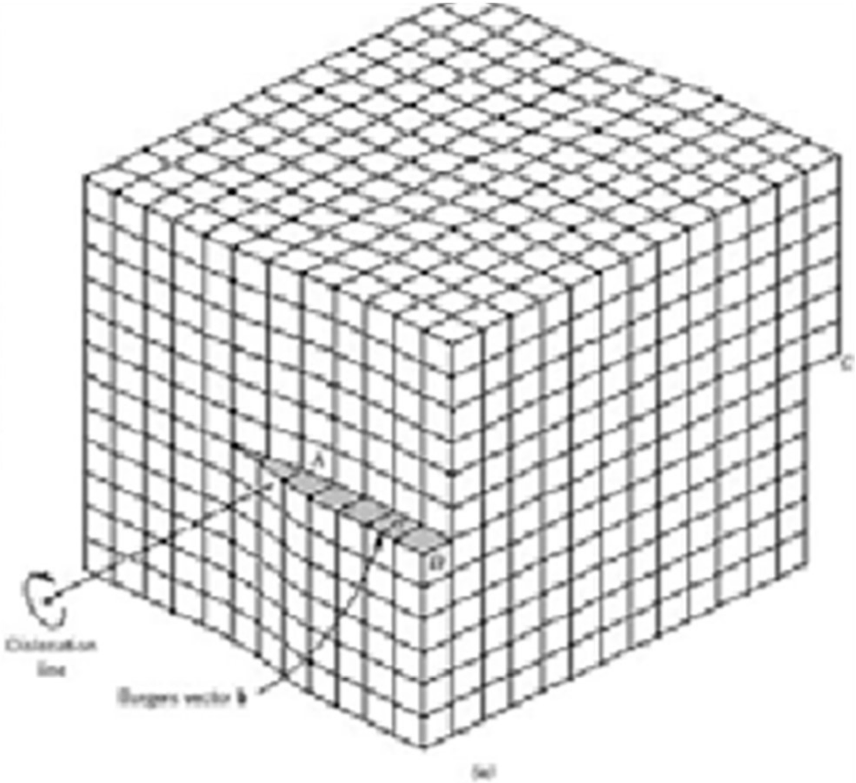


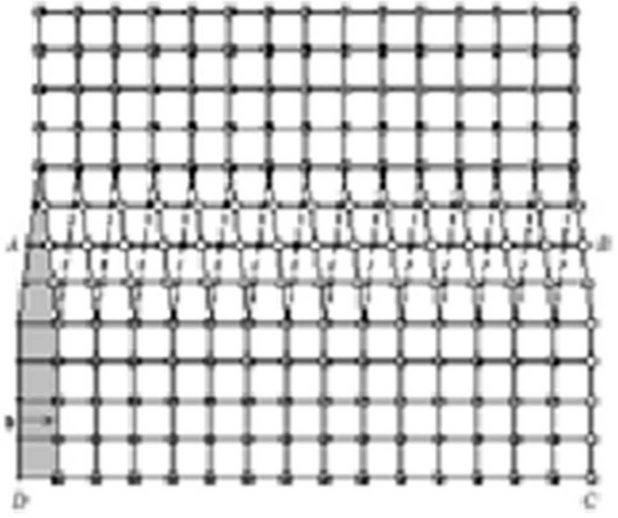
Edge dislocation



Screw Dislocation

- Formed by shear stress
- Also linear and along a dislocation line





7.2 Symmetry in crystal structures.

7.2.1 Symmetry elements and symmetry operations

- **Crystallographers make use of all the symmetry elements available in a crystal to minimize the number of independent coordinates.**
- **Three types of symmetry elements in a crystal lattice:**
- **Lattice symmetry (translational symmetry)**
- **Point symmetry (rotation, inversion & reflection etc.)**
- **Other translational symmetry elements: screw axes and glide planes**

a. Lattice symmetry
--- translation operation

$T_{mnp} = m\mathbf{a} + n\mathbf{b} + p\mathbf{c}$ or

$$T_{mnp} = \begin{pmatrix} m & 0 & 0 \\ 0 & n & 0 \\ 0 & 0 & p \end{pmatrix} \begin{pmatrix} \vec{a} \\ \vec{b} \\ \vec{c} \end{pmatrix}$$

a, b, c: basic vectors!

All unique translation operations available in a crystal lattice constitute a translation group $\{T_{\mathrm{mnp}}\}$ (order = ∞).

b. Point symmetry elements compatible with 3D translations

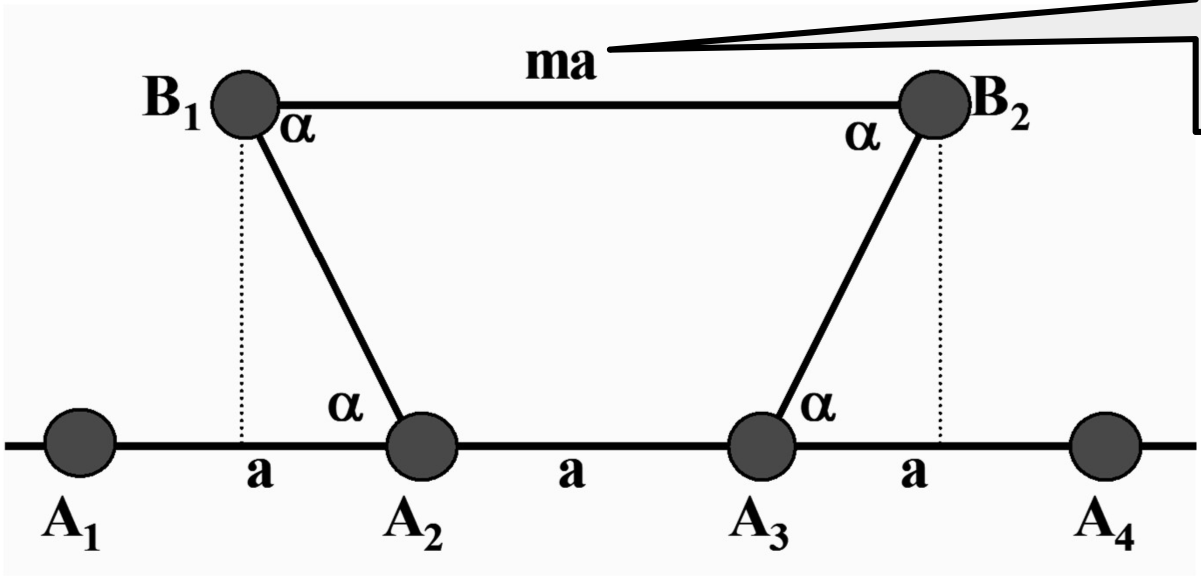
- A point-symmetry operation does not alter at least one point that it operates on, e.g., rotation, reflection, inversion, and rotation-inversion.

- Point symmetry elements available in a lattice must be compatible with the 3D translations, including

Operation	**Point symmetry elements**	
Reflection	**Mirror Plane**	m
Rotation operation	**Rotation axis**	$n = 1, 2, 3, 4, 6$
Inversion	**Center of symmetry**	$\bar{1}$
Rotatory inversion	**Inversion axis**	$\bar{3}, \bar{4}, \bar{6}$

It is provable that translational symmetry of a lattice excludes the presence of 5-fold axis!

Rotation axis: 1,2,3,4,6 only!! Why ???



Limitation induced by Translation symmetry!

Four lattice points: A_1, A_2, A_3, A_4

Upon an *n*-fold rotation,

$A_1 \longrightarrow B_1$

$A_4 \longrightarrow B_2$

with $A_1A_4 // B_1B_2$.

$B_1B_2 = a + 2a\cos\alpha = ma$

$\cos\alpha = (m-1)/2$

→ $\left|(m-1)/2\right| \leq 1$ → $\left|m-1\right| \leq 2$

→ $m = 3, 2, 1, 0, -1$

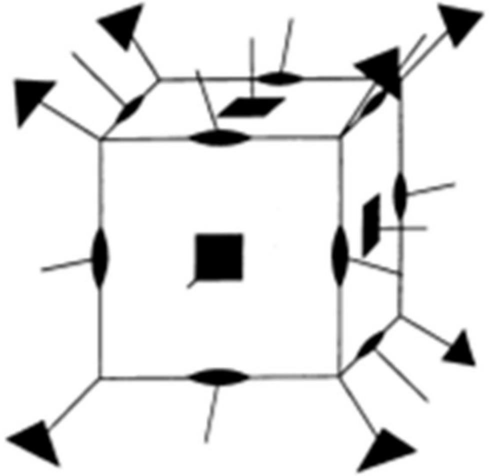
→ $\cos\alpha = 1, 1/2, 0, -1/2, -1$

→ $\alpha = 2\pi/n = 0°, 60°, 90°, 120°, 180°$

→ $n = 1,\ 6,\ 4,\ 3,\ 2$

rotation axes: 1,2,3,4,6 only!!

Example: The symmetry elements in a primitive cell of a cubic lattice.

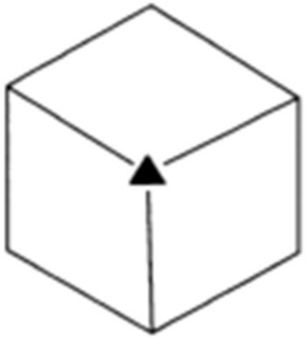


- ⬬ **Twofold axis**
- ▲ **Threefold axis**
- ■ **Fourfold axis**

⬮	▲	■	⬢
2	3	4	6

Rotation axis

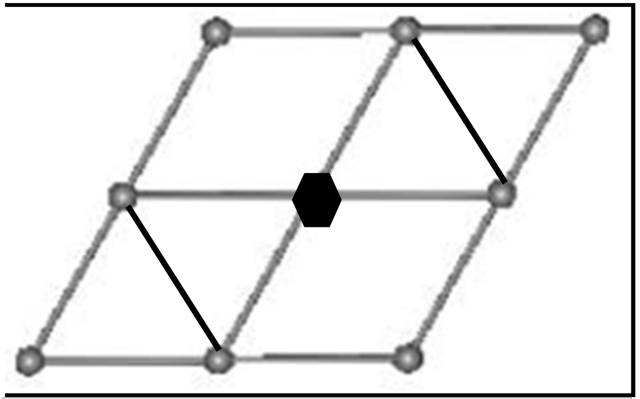
twofold axis



threefold axis

fourfold axis

Hexagonal lattice



Sixfold axis

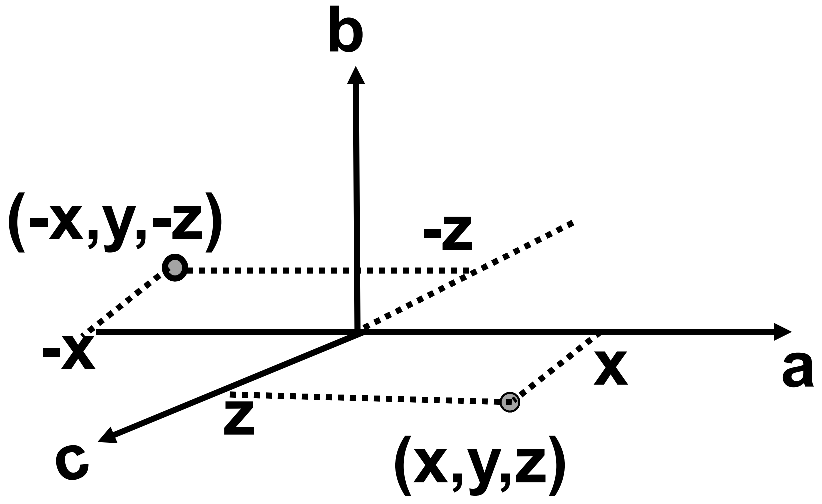
General equivalent positions:

i) 2-fold axis (e.g., *b* axis in monoclinic lattice)

(x, y, z) → (-x, y, -z) (Note: in fractional coordinates)

Equivalent upon rotation around a 2-fold axis.

$$R(2)=\begin{bmatrix}\bar{1} & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & \bar{1}\end{bmatrix}$$



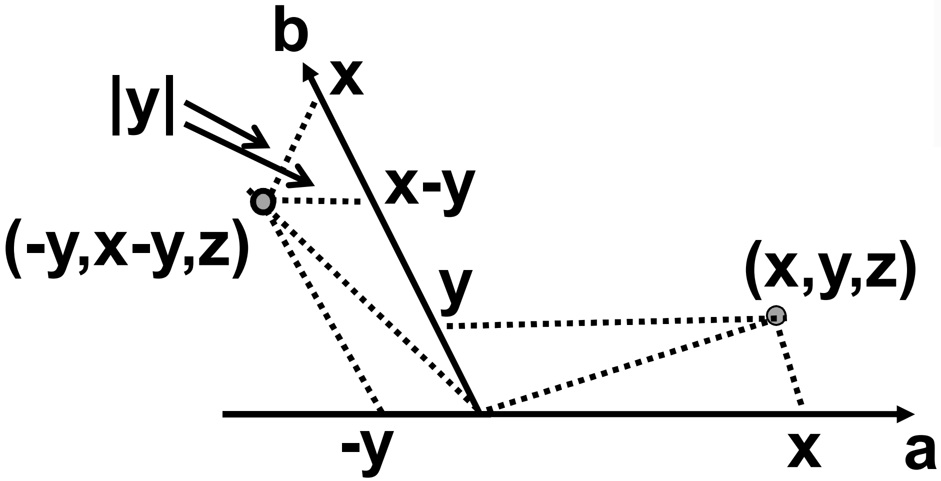
Note: β is not essentially 90°.

General equivalent positions:

ii) 3-fold axis //c axis in a hexagonal lattice

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

$$R(3) = \begin{bmatrix} 0 & \bar{1} & 0 \\ 1 & \bar{1} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$



$$R(4)=\begin{bmatrix}0 & \bar{1} & 0\\ 1 & 0 & 0\\ 0 & 0 & 1\end{bmatrix}$$

4 fold axis // c axis (cubic lattice)

general equivalent positions:

(x,y,z), (-y, x, z), (-x,-y,z), (y,-x,z)

$$R(6)=\begin{bmatrix}1 & \bar{1} & 0\\ 1 & \bar{1} & 0\\ 0 & 0 & 1\end{bmatrix}$$

6 fold axis // c axis (hexagonal lattice)

general equivalent positions:

(x,y,z), (x-y, x, z), (-y, x-y, z),

(-x,-y,z), (y-x, -x, z), (y, y-x,z)

c. Screw axes n_m (m<n) and glide planes:

A ***screw axis*** symmetry is combination of ***rotation about an axis*** and a ***translation*** parallel to that axis leaves a crystal unchanged.

Screw operation $\mathrm{n_m} = T\left(\frac{m\vec{a}}{n}\right)\cdot C_n^1 \quad (C_n // \vec{a},\ \ m = 1,2,\ldots,n-1)$

An n-fold screw axis can be n_1, n_2, …, or n_{n-1}.

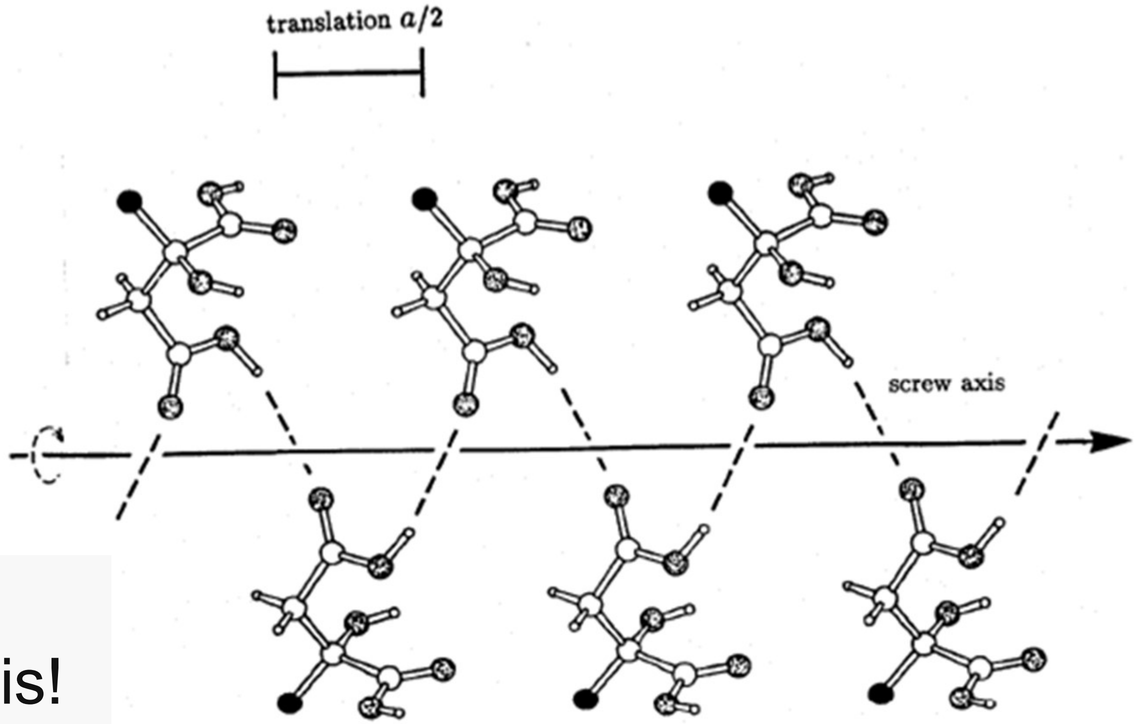
Example: 2_1// ***a*** axis

$$(x, y, z) \xrightarrow{C_2(//\boldsymbol{a})}$$

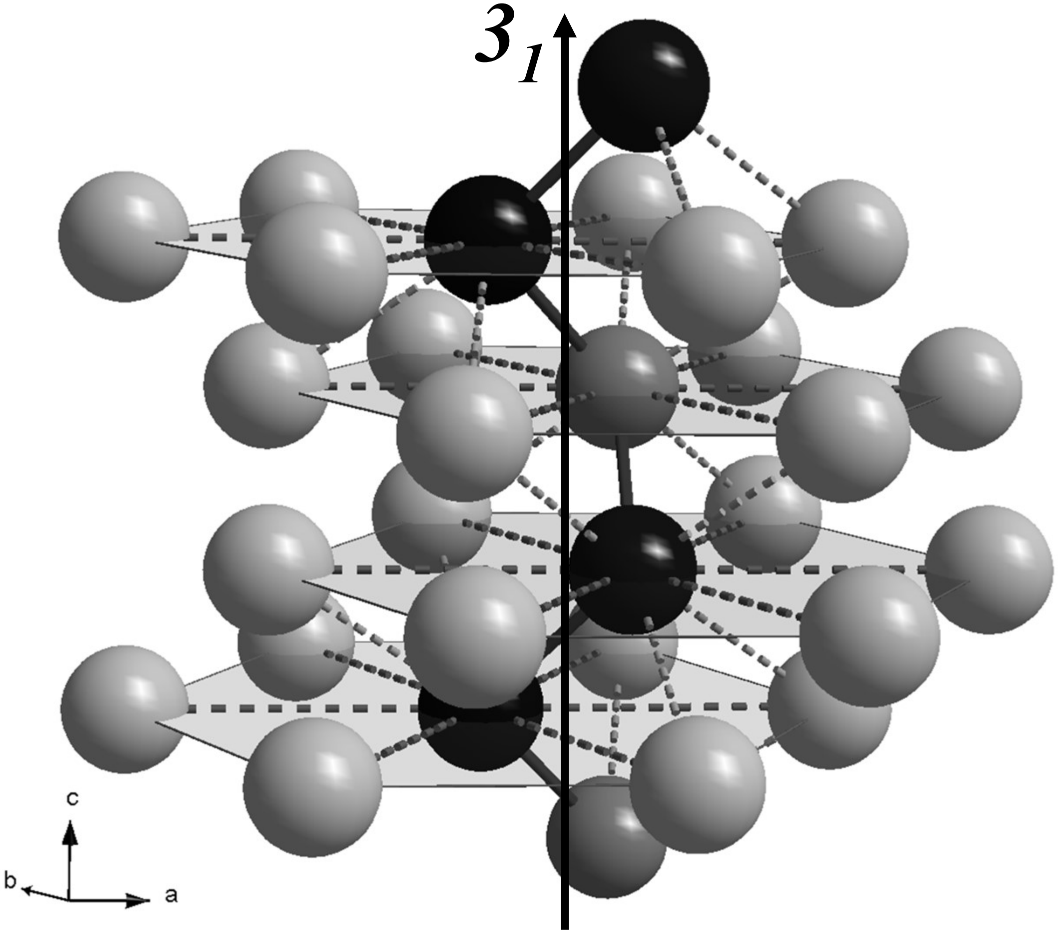
$$(x, -y, -z) \xrightarrow{T(a/2)}$$

$$(x+1/2, -y, -z)$$

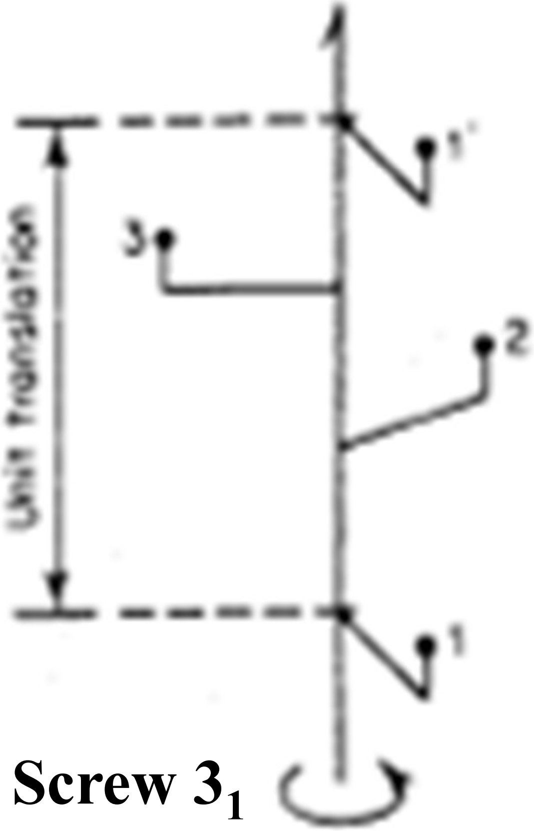
A helical structure is related to a screw axis!



A 3_1 screw axis in the crystal of tellurium

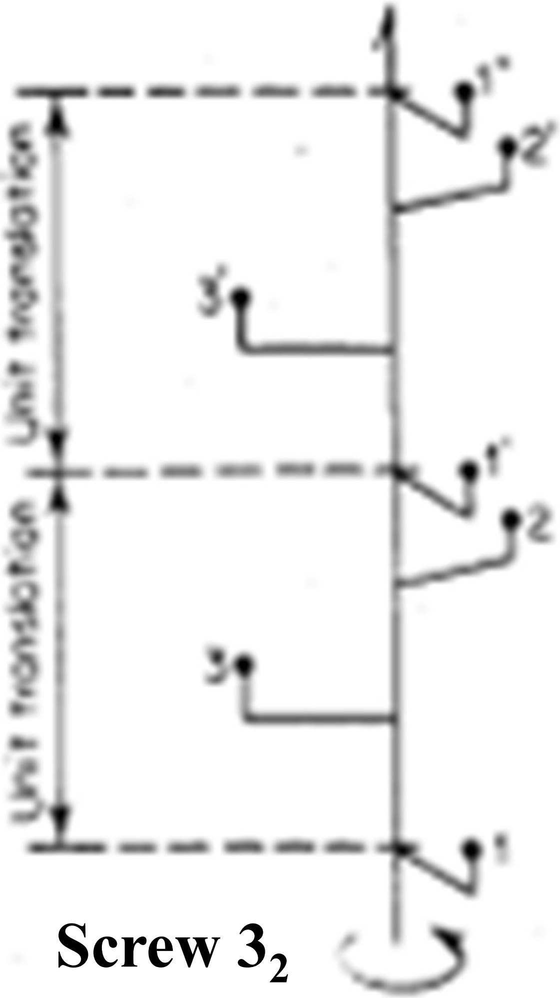


Screw axes: 3_1 and 3_2



Screw 3_1

= T(a/3) C_3^1

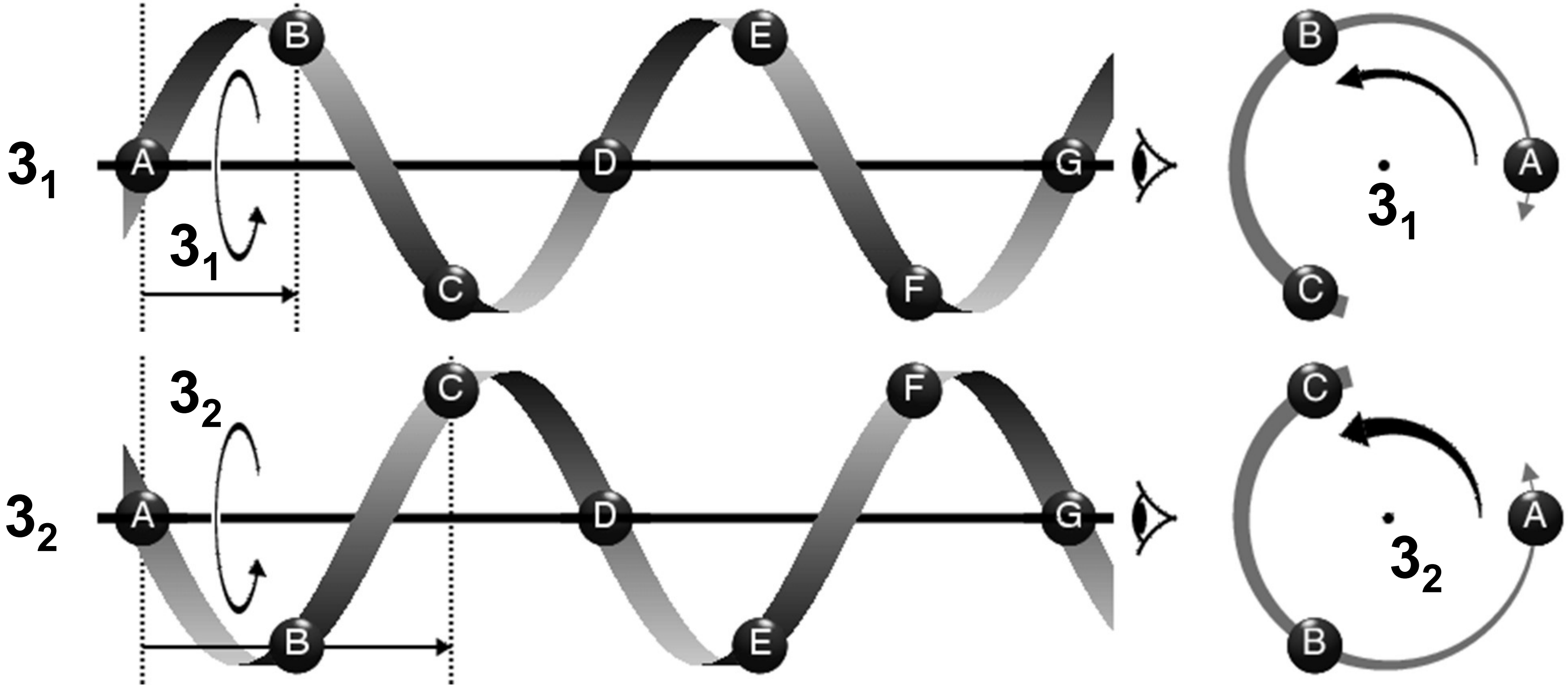


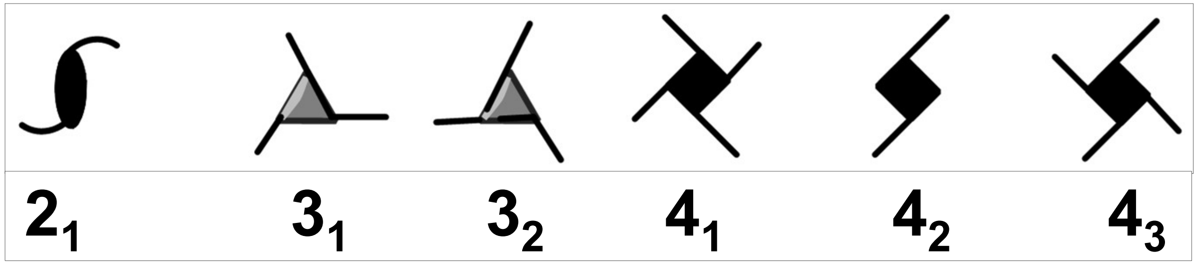
Screw 3_2

= T(2a/3) C_3^1

Helical structures along screw axes

View perpendicular to axis **View down axis**





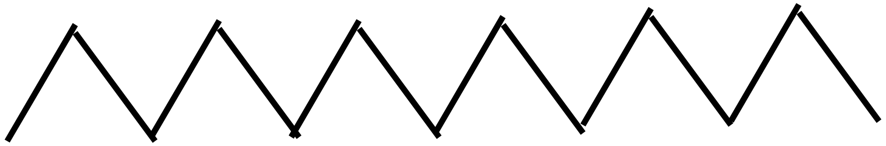
$6_{1\text{-}5}$

Glide operations: *a*, *b*, *c*, *n* and *d* glides

Glide operation: G = T(t)·M   Mirror: M (reflection)

t = a/2, b/2, c/2, (a+b)/2, (b+c)/2, (a+c)/2, (a+b+c)/4 etc.

GG = $[T(t)M]^2 = T(2t)$, τ = 2t (maybe a basis vector of lattice)



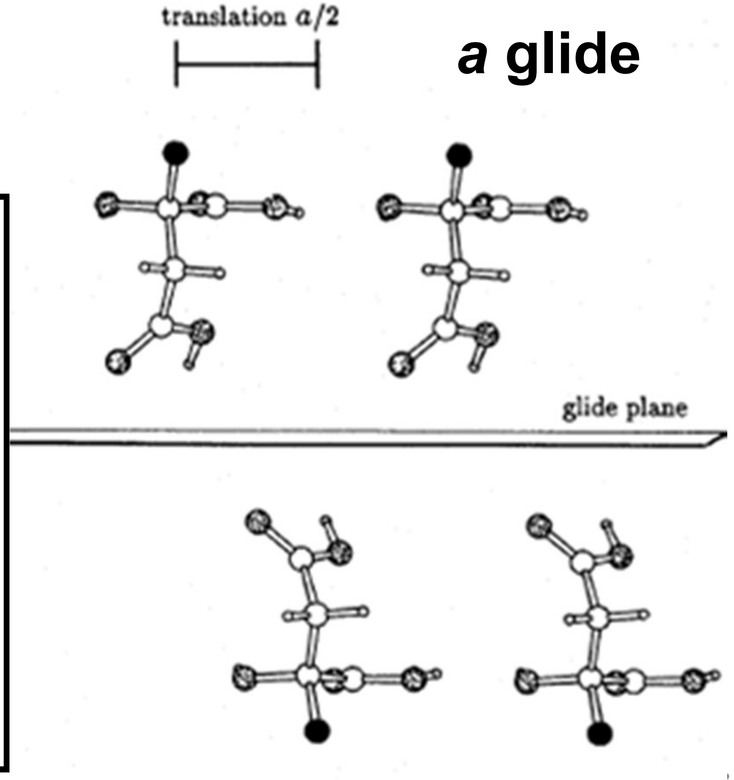
Zig-zag structure

***a,b,c glide*: *t* = a/2 , b/2, c/2**

n glide: *t* =(a+b)/2, (b+c)/2, (a+c)/2

d glide: *t*= (a+b+c)/4, (a+b)/4, (b+c)/4, or (a+c)/4 .

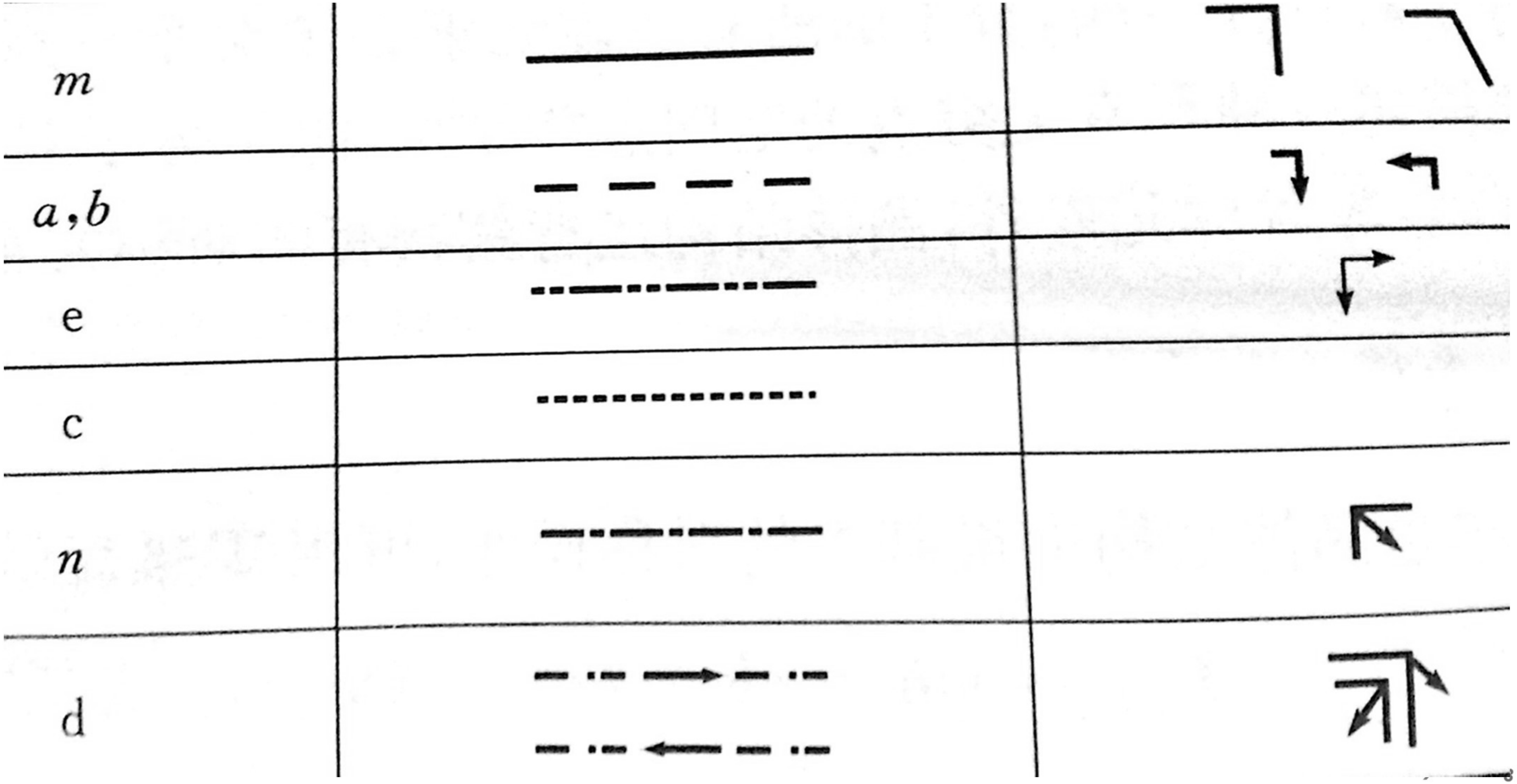
e glide (double glide plane).



***a* glide**

Graphical representations of glide and mirror planes

Type **Projection (⊥)** **Parallel (//)**



Summary of symmetry elements and symmetry operations in crystal structure

Symm. operation	Symm. Elements
• Rotation operation	rotation axis $\boldsymbol{C_n}$
• Reflection operation	mirror plane $\boldsymbol{m}$
• Inversion operation	inversion center
• Rotation inversion operation	inversion axis
• Translation operation	lattice
• Screw operation	screw axis $\boldsymbol{n_m}$
• Glide operation	glide plane

(n=1, 2, 3, 4, 6)

Combinations of the 8 point symm. elements (5 *n*-axis, *i*, *m*, S_4) result in 32 crystallographic point groups.

Combining symmetry elements

- When a crystal possesses more than one of the above point symmetry elements, these macroscopic symmetry elements must all pass through a common point.
- There are ***32*** possible combinations of the above symmetry elements that pass through a point.
- There are the ***32*** crystallographic point groups.
- So far we have

7 Crystal systems → 14 Bravais lattices (Translation) +

32 crystallographic point groups (Point symmetry)

→ 230 space groups

7.2.2 Crystallographic point group and space group

1. Crystallographic point group

Combinations of the 8 point symm. elements (5 *n*-axis, *i*, *m*, S_4) result in 32 crystallographic point groups.

e.g., Monoclinic system: point symmetry elements -- **2**, **m**,

2 – **{E, C_2}** -- C_2 point group; ***m*** - **{E,σ}** -- C_s point group.

2,m -- ***{E, C_2, σ, i}*** -- C_{2h} point group.

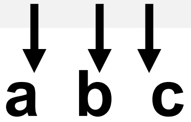
Two notations of crystallographic point group

Schonflies notation vs. International notation

C_2	*2*
C_S	*m*
C_{2h}	*2/m*

- Each crystal system includes a set of distinctive crystallographic point groups.
- A total of 32 crystallographic point groups.

Crystal system	Schonflies notation	International notation	Symmetry elements	Examples
monoclinic	C_2	2	C_2	$BiPO_4$
	C_S	m	σ	KNO_2
	C_{2h}	2/m	C_2, σ_h, i	$KAlSi_3O_8$
orthorhombic	D_2	222	$3C_2$	HIO_3
	C_{2v}	mm2	C_2, 2σ	$NaNO_2$
	D_{2h}	mmm	$3C_2$, 3σ, i	$MgSO_4$



2. Crystallographic space group

Point groups (32) + translational symmetries = Space groups (230)

Schonflies notation vs. International notation

e.g, $\mathbf{D_{2h}^{16}}$ **- $\mathbf{P2_1/n\ 2_1/m\ 2_1/a}$** $\mathbf{C_{2h}^{5}}$ **– $\mathbf{P2_1/c}$**

System		**directions**	
	1	**2**	**3**
Cubic	**a**	**a+b+c**	**a+b**
Hexagonal	**c**	**a**	**2a+b**
Tetragonal	**c**	**a**	**a+b**
Trigonal (hR)	**a+b+c**	**a-b**	**-**
Trigonal* (hP)	**c**	**a**	
Orthorhombic	**a**	**b**	**c**
Monoclinic	**b**	**-**	**-**

How to understand/use Space Group?

Symmetry elements & equivalent positions

1. Each space group can be schematically represented by using two types of diagrams, i.e., diagrams of symmetry elements and diagram of general equivalent positions.

2. The physical meaning of general equivalent positions: if there is an X atom at position (x,y,z), there should a same X atom at each equivalent position within a unit cell.

Diagram of Symmetry elements

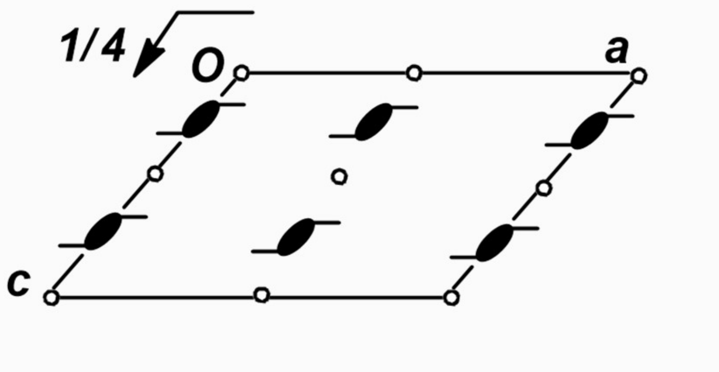
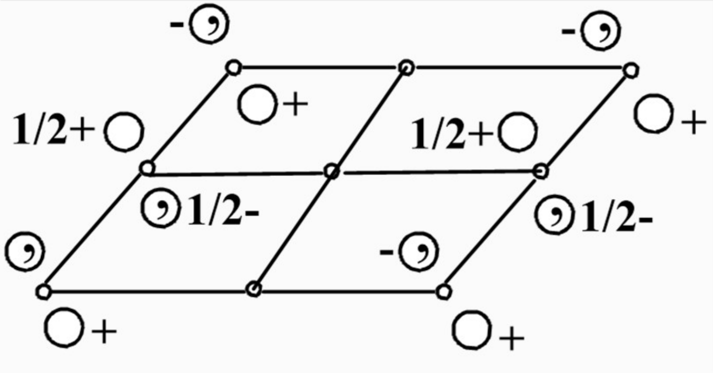


Diagram of general equivalent position



Example: monoclinic point group C_{2h}-2/m

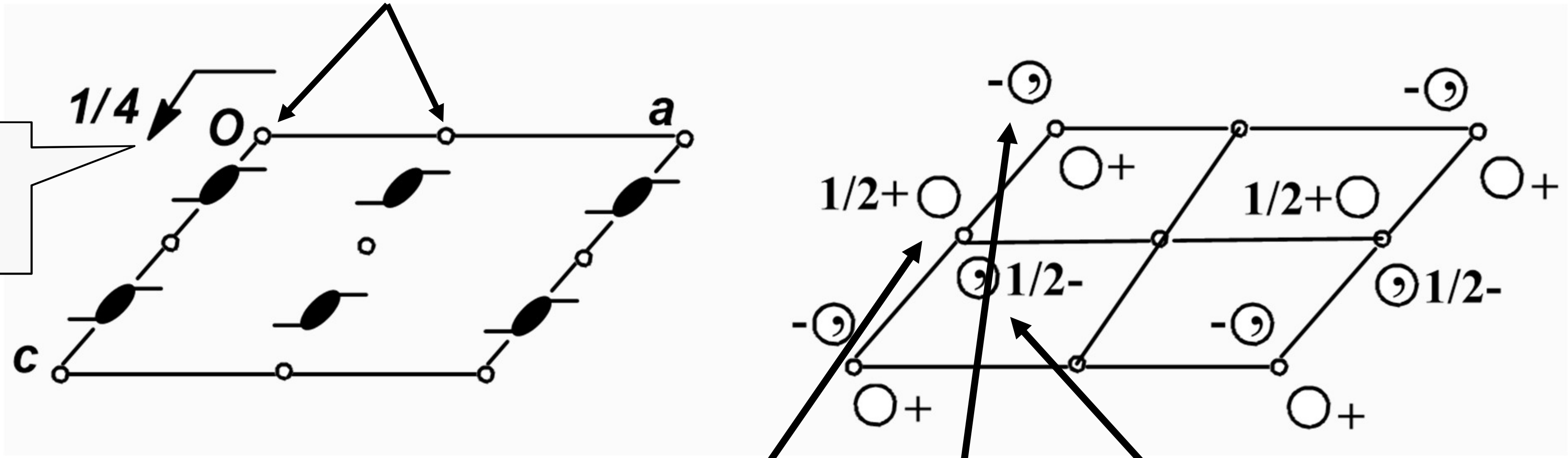
Six space groups belong to C_{2h} point group, denoted:

C_{2h}^1-P2/m, C_{2h}^2-P2_1/m, C_{2h}^3-C2/m,

C_{2h}^4-P2/c, C_{2h}^5-P2_1/c, C_{2h}^6-C2/c,

e.g., C_{2h}^5 – P2_1/c (***i*** is always available!)

c glide at b/4.



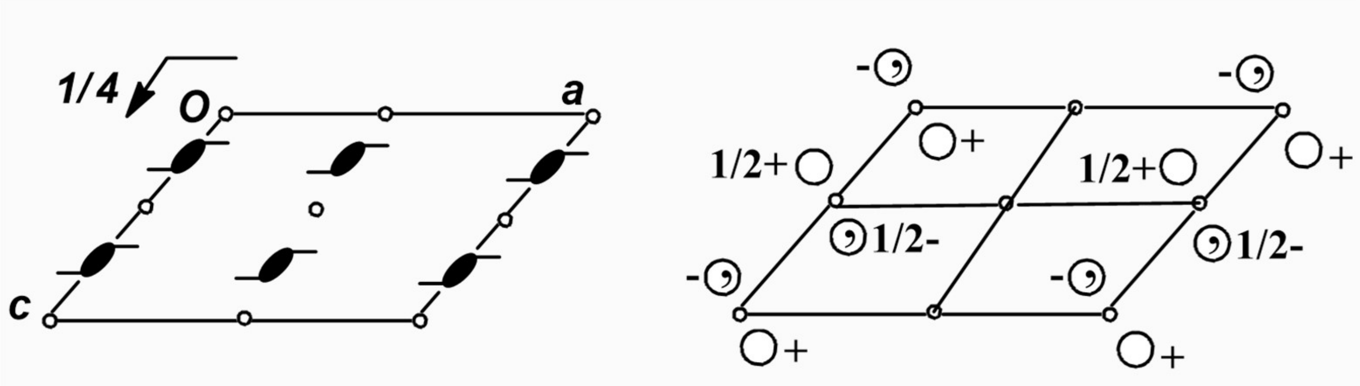
A set of equivalent positions located within a unit cell!

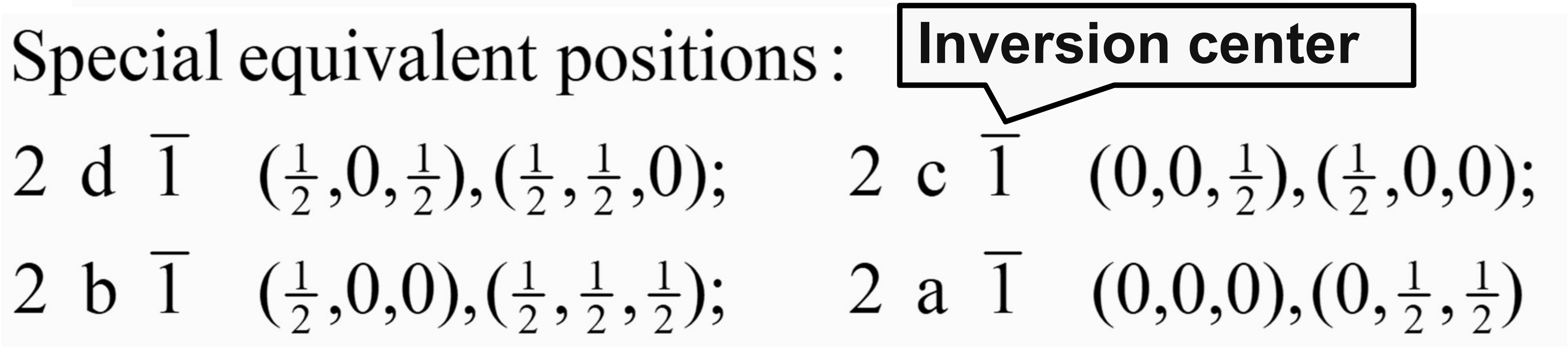
General equivalent positions:

4 e 1 (x, y, z), (-x, y + 0.5, 0.5 – z), (-x, – y, – z), (x, 0.5 – y, 0.5 + z)

Multiplicity, Wyckoff letter, site symmetry

e.g., C_{2h}^5 – $P2_1/c$





Special equivalent positions:

Inversion center

$2\ \mathrm{d}\ \bar{1}\quad (\frac{1}{2},0,\frac{1}{2}),(\frac{1}{2},\frac{1}{2},0);\qquad 2\ \mathrm{c}\ \bar{1}\quad (0,0,\frac{1}{2}),(\frac{1}{2},0,0);$

$2\ \mathrm{b}\ \bar{1}\quad (\frac{1}{2},0,0),(\frac{1}{2},\frac{1}{2},\frac{1}{2});\qquad 2\ \mathrm{a}\ \bar{1}\quad (0,0,0),(0,\frac{1}{2},\frac{1}{2})$

- **Equivalent positions are correlated by symmetry elements and can be produced from a given position upon available symmetry operations.**
- **Thus it is unnecessary to list all atoms, but unique type of atoms within a unit cell.**

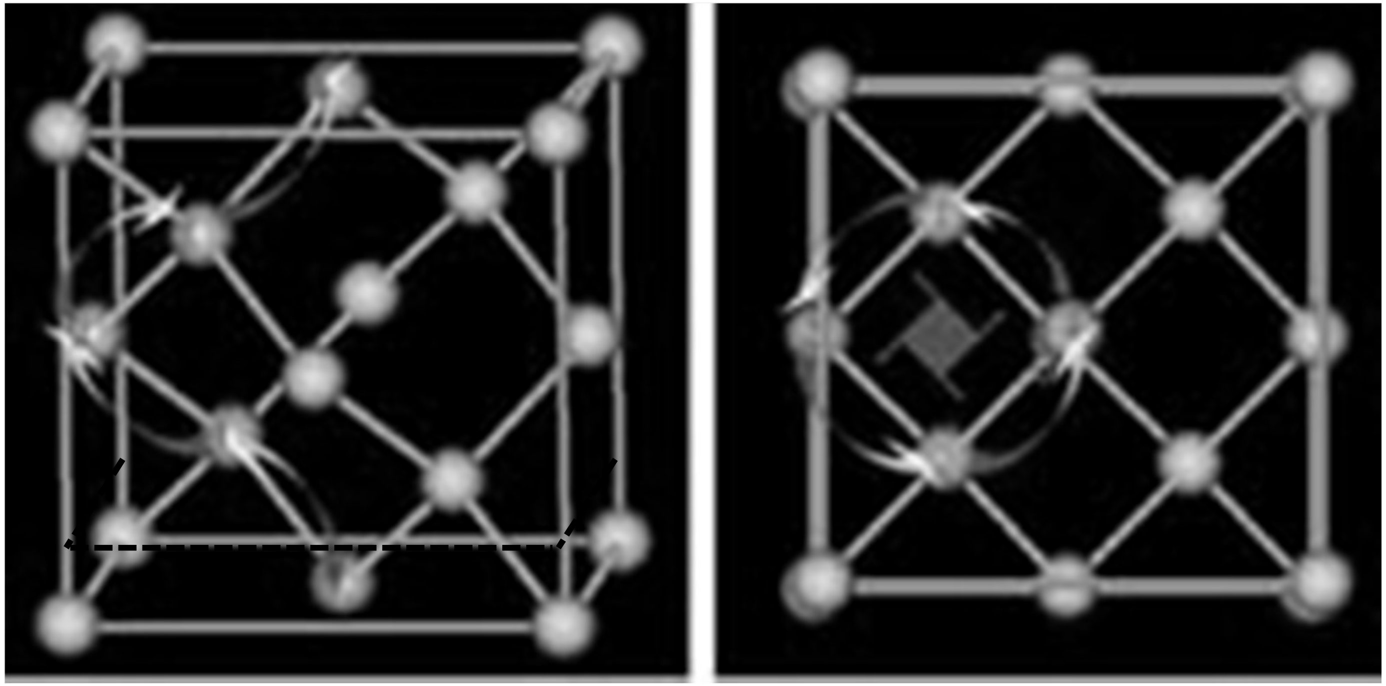
Diamond: face-centred cubic O_h^7- $Fd\bar{3}m$

4_1

d glide plane at

1/8,3/8,

5/8,8/7



Sideview topview

- **Fcc**
- **Lattice points: (0,0,0)+, (1/2,1/2,0)+, (0,1/2,1/2)+, (1/2,0,1/2)+**
- **Structure motif – 2C 0,0,0; 1/4,1/4,1/4**
- **Totally 8 C atoms within a unit cell.**

Note：In this case, the presence of same-type atoms in structure motif introduces more symmetry elements!

7.2.3 The description and application of crystal structure

Example 1. Crystal of iodine

Crystal System orthorhombic

Space group **D_{2h}^{18}-Cmca (or C 2/m 2/c 2_1/a)**

Cell parameters a=713.6 pm b= 468.6 pm c = 987.4 pm

Number of molecules per unit cell ***Z = 4***

Atomic coordinate for I	x	y	z
	0	0.15434	0.11741

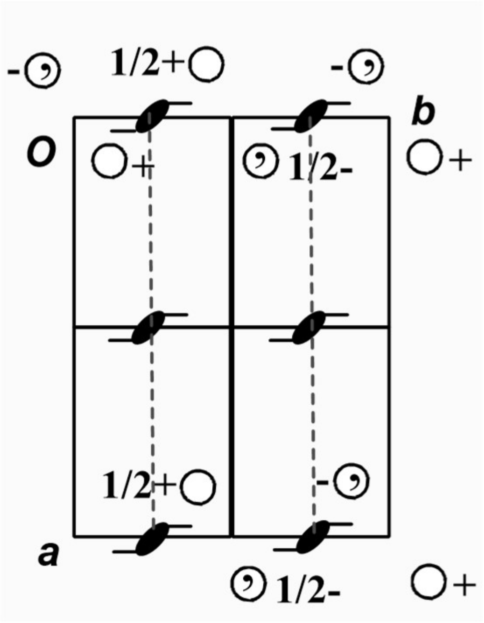
Lattice points within a unit cell: **(0,0,0)+, (1/2, 1/2, 0)+ (C-centered)**.

General equivalent positions:

C 2/m 2/c 2_1/a

(x,y,z); (-x, -y, -z); (-x, -y+1/2, z+1/2); (x, y+1/2, -z+1/2)

(0, .15434, .11741)	**(1/2, .65434, .11741)**
(0, -.15434, -.11741)	**(1/2, .34566, -.11741)**
(0, .34566, .61741)	**(1/2, .84566, .61741)**
(0, .65434, 38259)	**(1/2, .15434, 38259)**



a) Bond length (Bond distance)

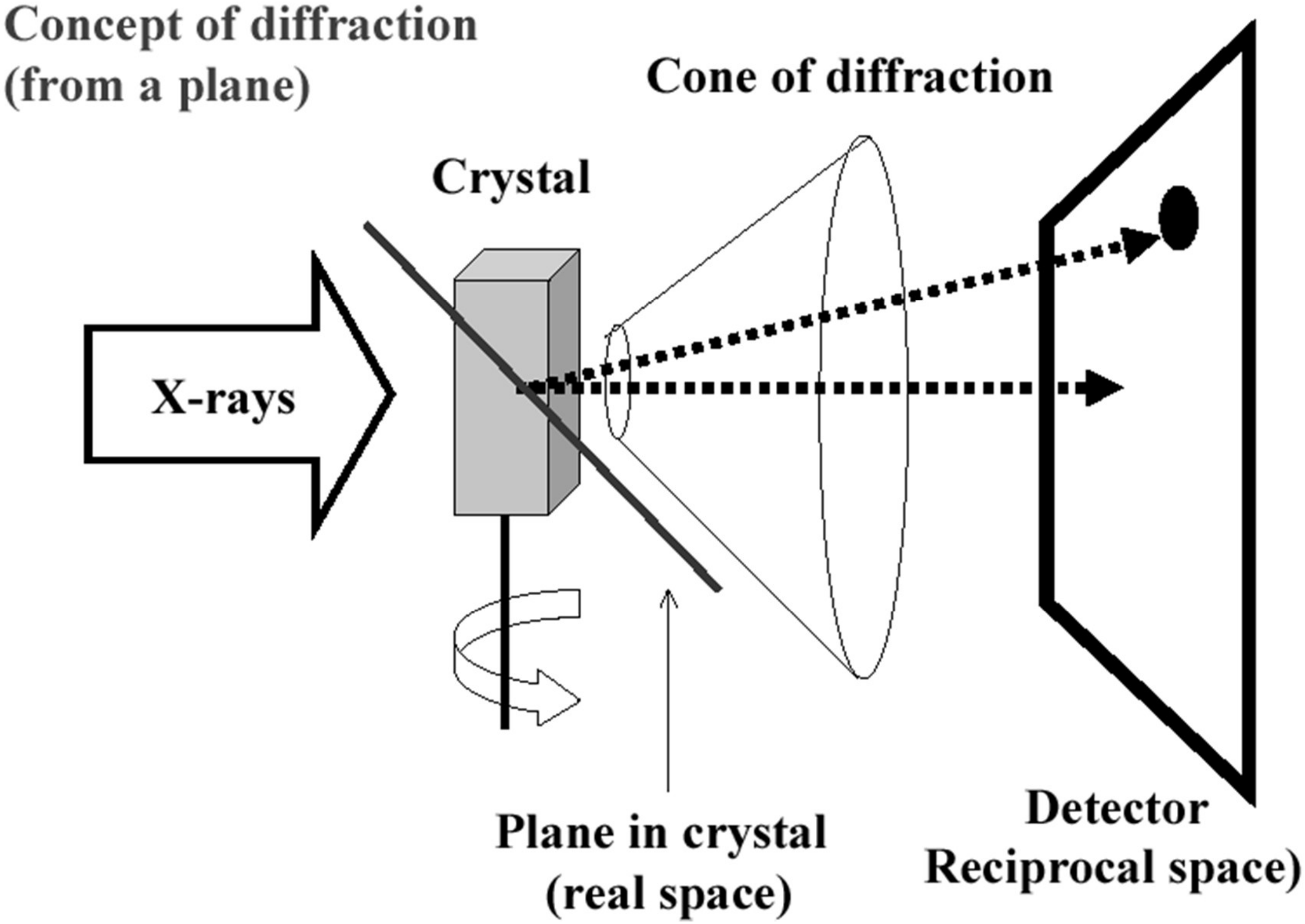
$$r_{1\text{-}2} = [(x_1-x_2)^2a^2+(y_1-y_2)^2b^2+(z_1-z_2)^2c^2]^{1/2} = 2.715\ \text{Å}$$

b) Density of crystal

$$V = a \times b \times c = 3.27 \times 10^8\ \text{pm}^3$$

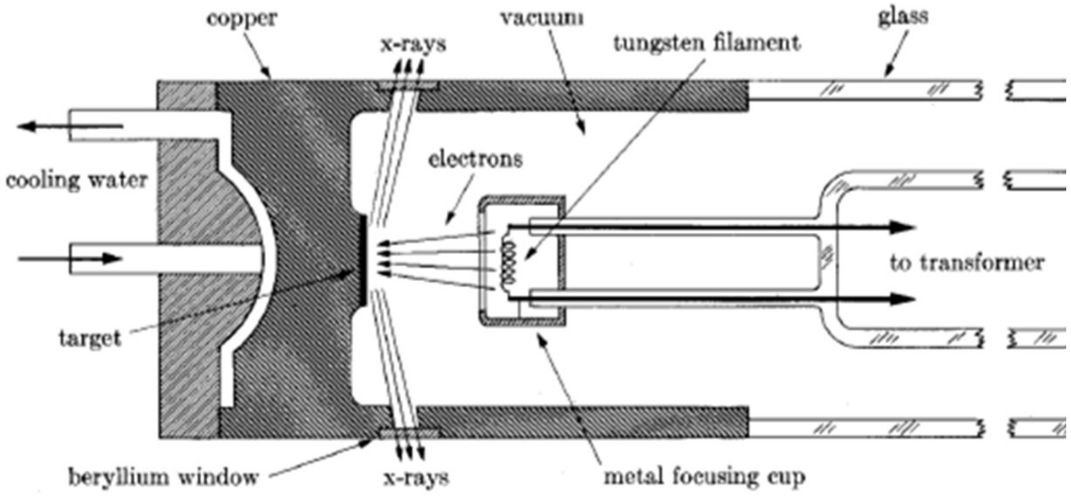
$$D = 8 \times 127.0 /(6.02 \times 10^{23} \times 327.0 \times 10^{-24})\ \text{g cm}^{-3} = 5.16\ \text{g cm}^{-3}$$

7.3 X-ray diffraction of crystals

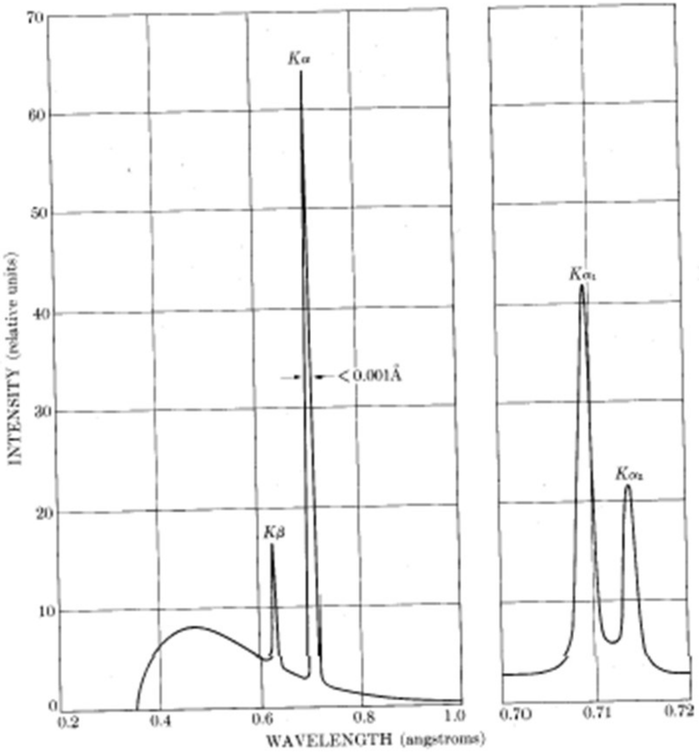


The wavelengths (0.05-2.5 Å) of x-rays match the d-spacing of crystal planes, resulting in diffraction!

7.3.1 The source and property of X-ray



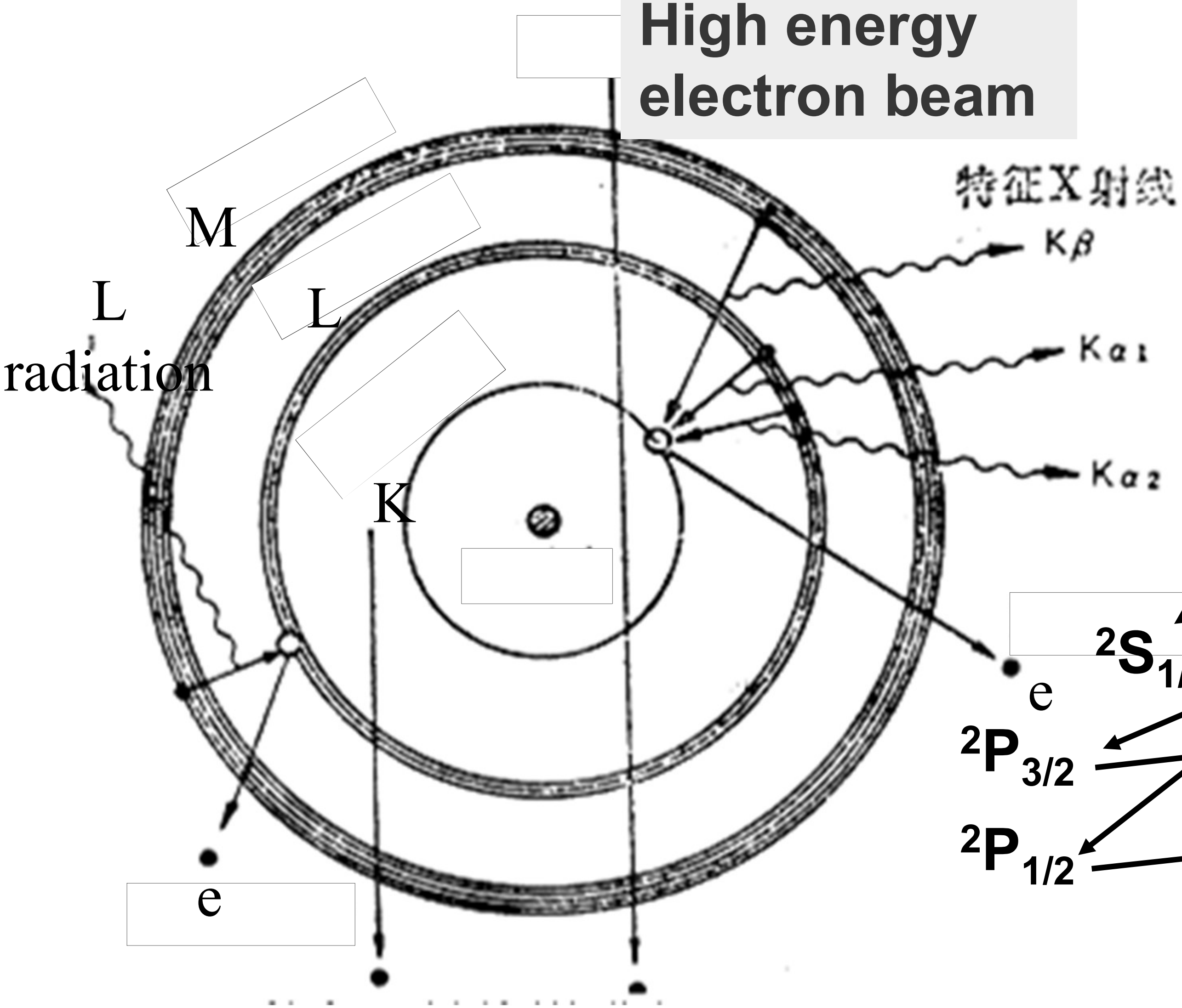
X-ray tube



The wavelengths of X-ray are in the range of 100-0.01Å

- **1-0.01Å: hard x-ray**
- **100～1Å：soft x-ray**
- **2.5-0.5Å: used in crystal structure analysis**
- **1-0.05Å: used in medical perspective, detection of materials wound**

X-rays produced by electronic transition between atomic energy levels



High energy electron beam

A part of the electrons are blocked; their kinetic energies giving rise to "white" x-ray.

As for Cu:

Cu$^+$ $1s^1 2s^2 2p^6$…

→ $1s^2 2s^2 2p^5$…

$^2S_{1/2}$

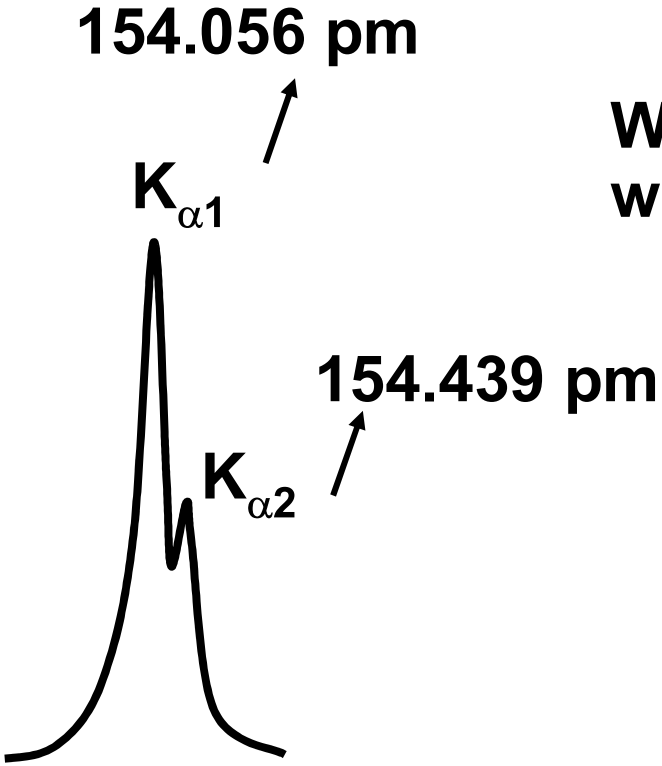
$^2P_{3/2}$

$^2P_{1/2}$

$K_{\alpha 1}$ = 1.540594 Å

$K_{\alpha 2}$ = 1.544422 Å

$I_{K\alpha 1} \approx 2I_{K\alpha 2}$



154.056 pm

$K_{\alpha 1}$

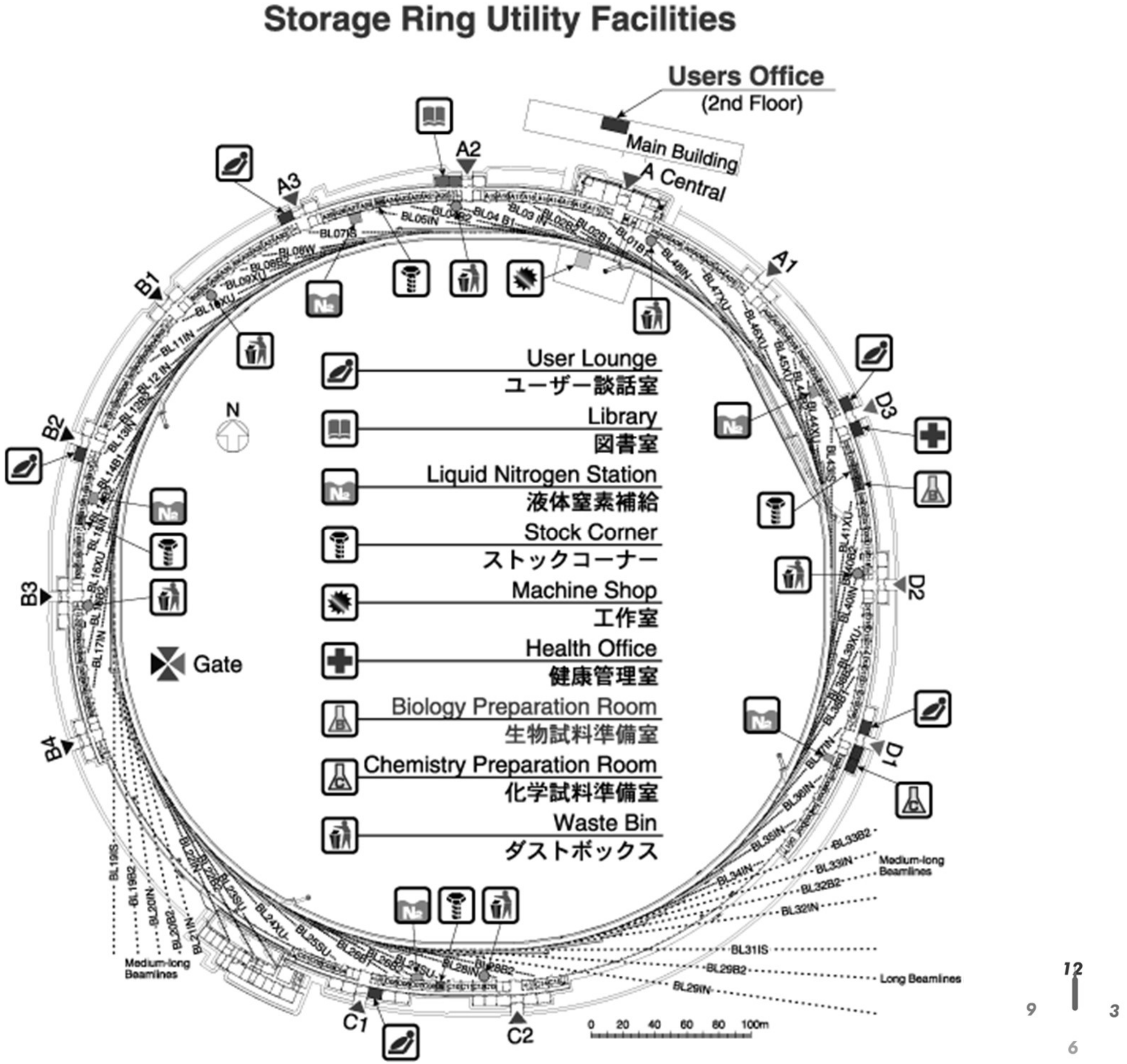
154.439 pm

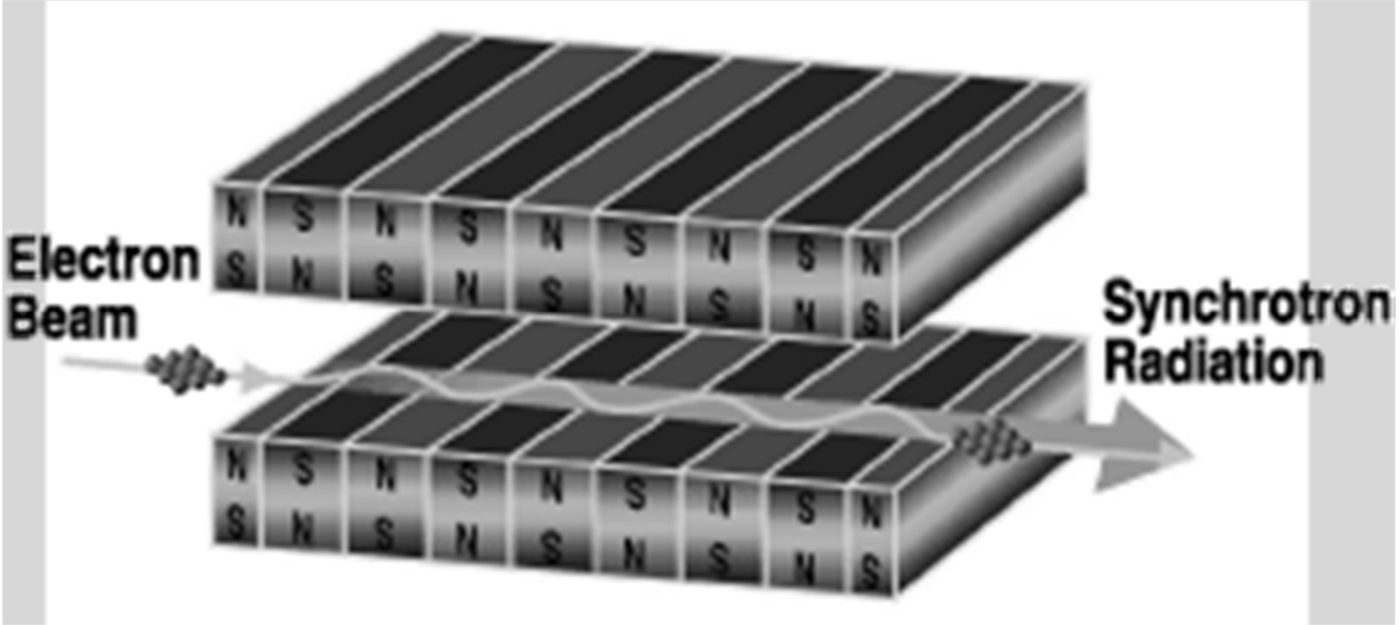
$K_{\alpha 2}$

Weighted average of wavelength ~ 154.18pm.

Note: $K_{\alpha 2}$ can not be striped by the monochromator.

Synchrotron Radiation X-ray Source

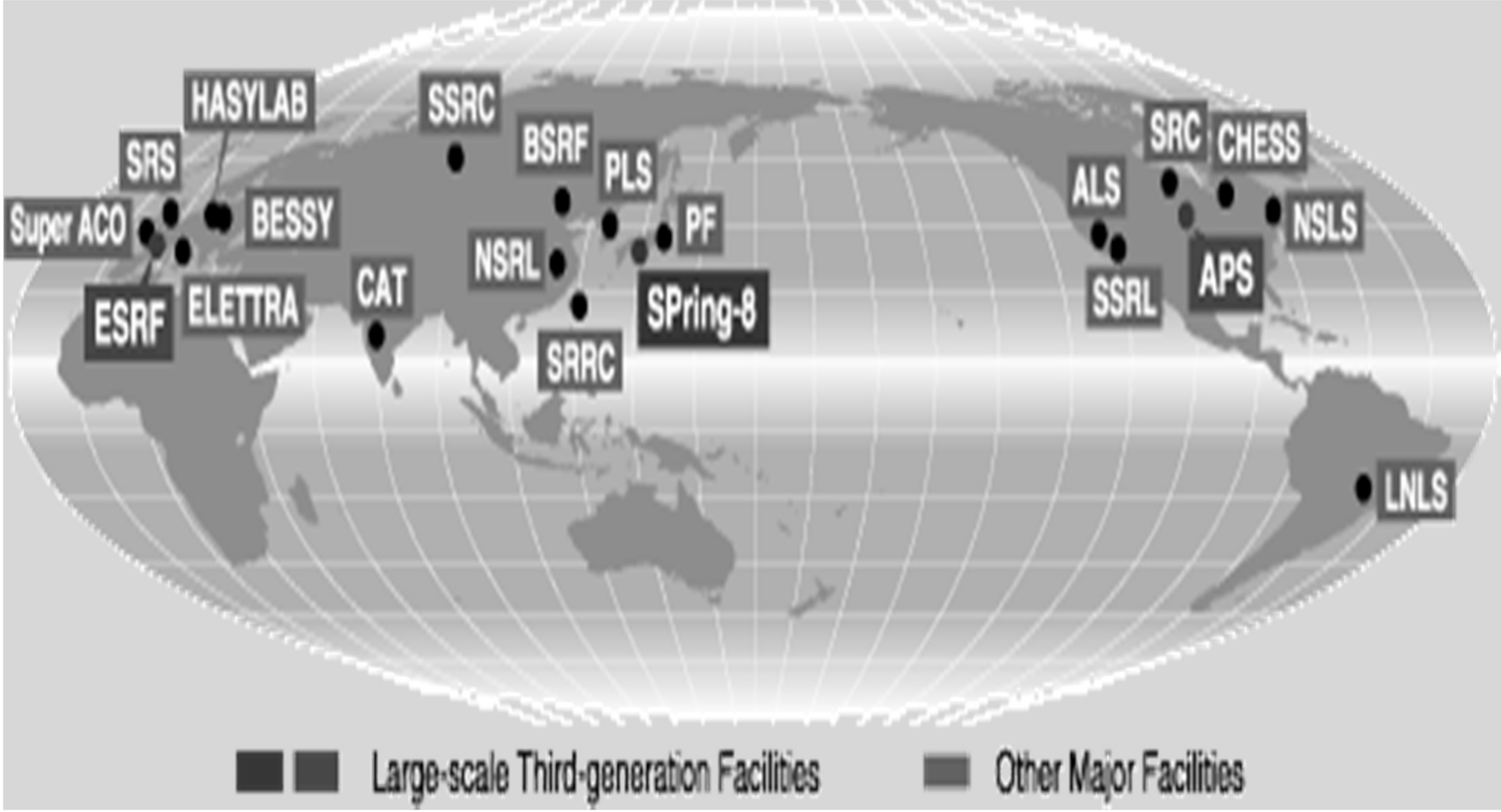




Benefits of Synchrotron radiation X-ray :

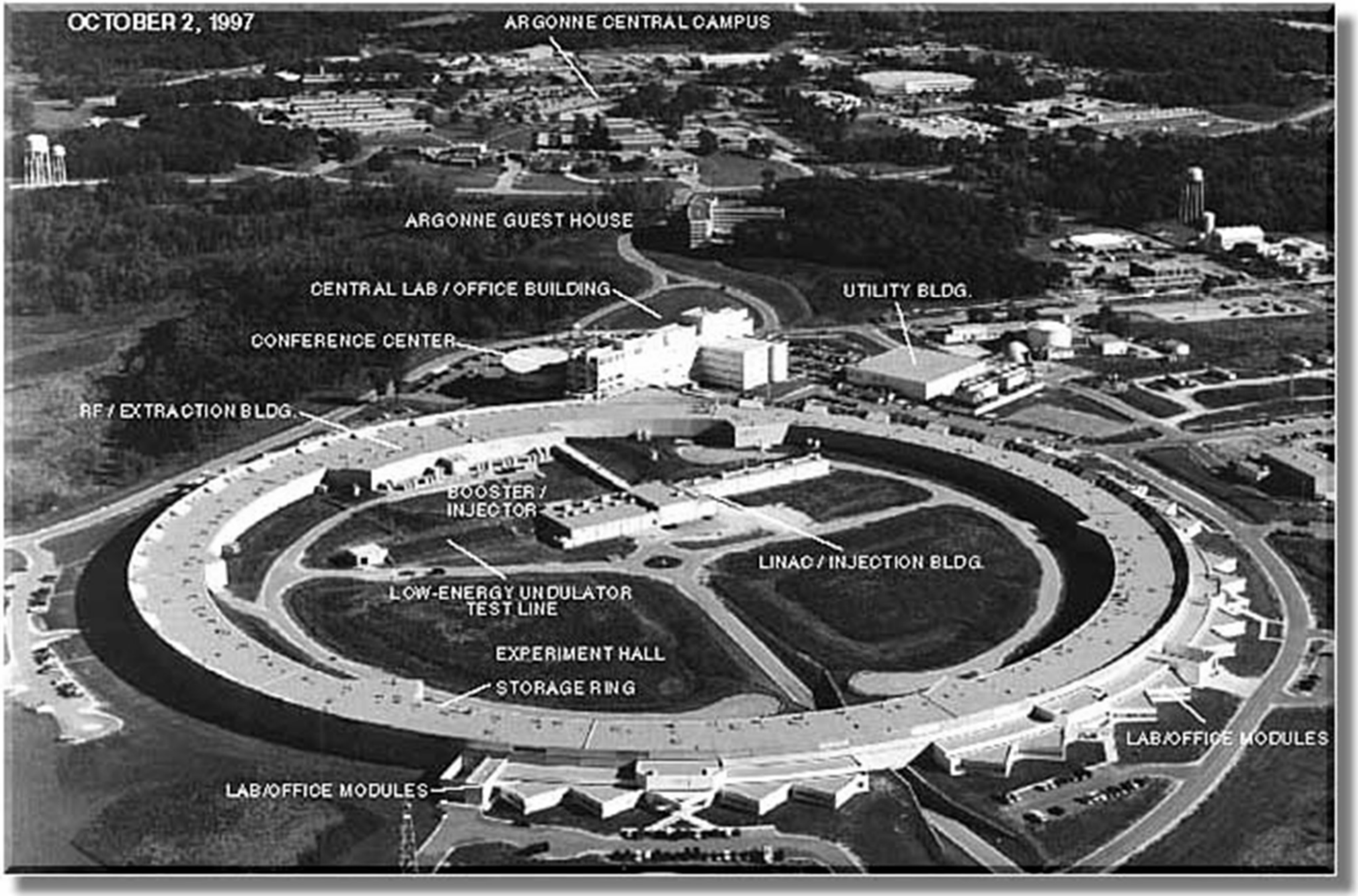
- **Narrow range of x-ray wave-lengths, i.e., high monochromicity**
- **High intensity of x-ray.**
- **High intensity and high quality of diffraction data**
- **High resolution – characterization microcrystals**

Toooooooo Expensive facility!


HASYLAB
SSRC
SRS
BSRF
PLS
SRC
CHESS
ALS
Super ACO
BESSY
PF
NSLS
NSRL
CAT
SPring-8
APS
SSRL
ESRF
ELETTRA
SRRC
LNLS
Large-scale Third-generation Facilities
Other Major Facilities

SPring-8, at Osaka, Japan. www.spring8.or.jp

ESRF - European Synchrotron Radiation Facility , Polygone Scientifique Louis Néel - 6, rue Jules Horowitz - 38000 Grenoble - France , http://www.esrf.fr



The Advanced Photon Source (APS) at Argonne National Laboratory, http://www.aps.anl.gov/aps.php

7.3.2 Laue equation and Bragg's Law

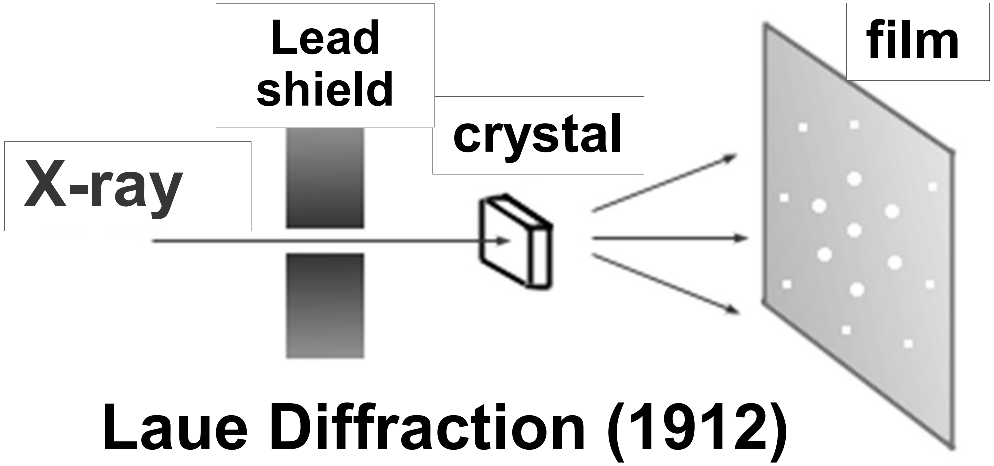
1. Laue equations

Laue first mathematically described diffraction from crystals.

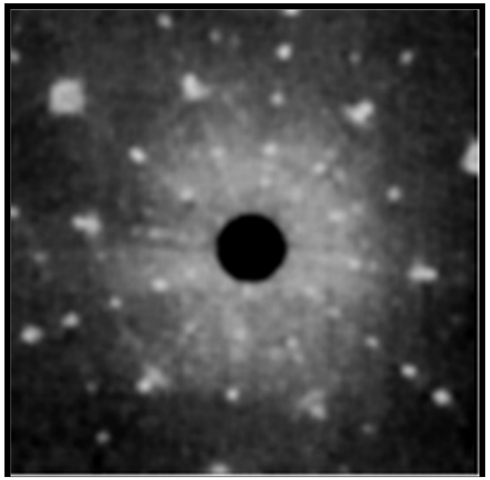
- consider X-rays scattered from every atom in every unit cell in the crystal. and how they interfere with each other
- to get a diffraction spot you must have constructive interference.

Max Von Laue

Nobel Prize in Physics 1914

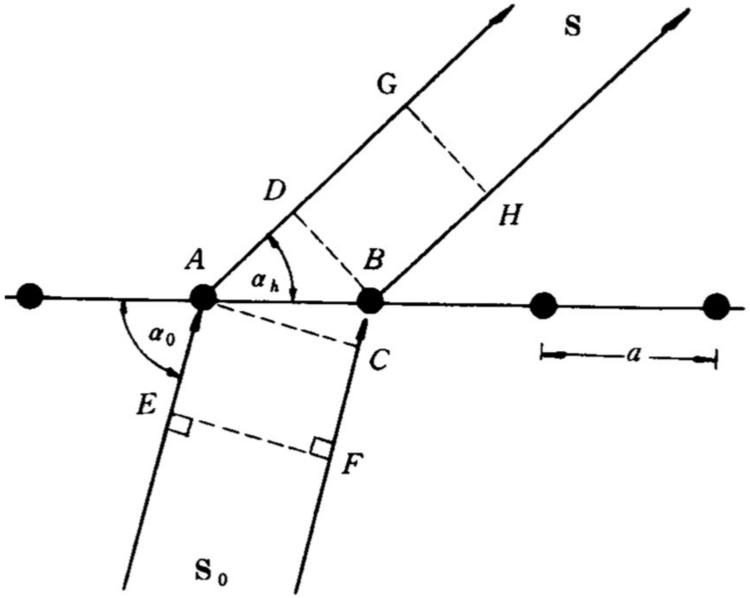


Laue Diffraction (1912)



Laue diffraction pattern of ruby

Laue equations (Based on diffraction by 1D atomic lattice)



a — lattice parameter

α_0— angle between ***a*** and ***S_0***

α — angle between ***a*** and ***S***

Interference condition:

The difference in path lengths of adjacent lattice points must be a multiple integral of the wavelength.

$$i.e., \Delta = AD\text{-}CB = h\lambda, h = 0, \pm1, \pm2, \ldots$$

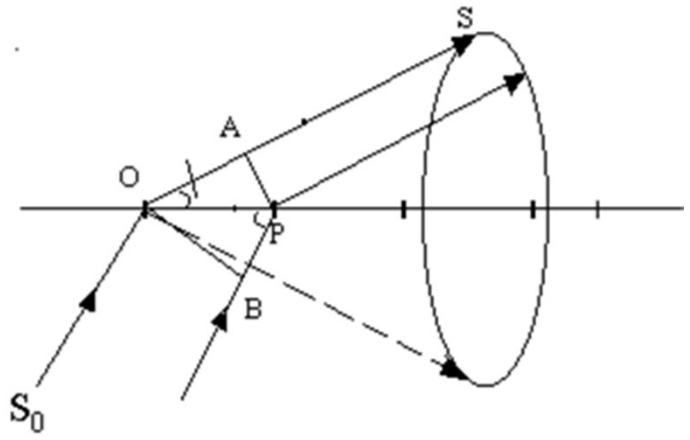
$$AD = \mathbf{a} \bullet \mathbf{S} = a\cos\alpha$$

$$CB = \mathbf{a} \bullet \mathbf{S}_0 = a\cos\alpha_0$$

$$\Delta = \mathbf{a} \bullet (\mathbf{S} - \mathbf{S}_0)$$

$$= a(\cos\alpha - \cos\alpha_0) = h\lambda$$

For each *h* value, the diffraction rays from a 1D lattice make a cone!



Expanded to 3D lattice case:

$$\left.\begin{array}{l}
\mathbf{a}\cdot(\mathbf{S}-\mathbf{S}_0) = a(\cos\alpha-\cos\alpha_0) = h\lambda \\
\mathbf{b}\cdot(\mathbf{S}-\mathbf{S}_0) = b(\cos\beta-\cos\beta_0) = k\lambda \\
\mathbf{c}\cdot(\mathbf{S}-\mathbf{S}_0) = c(\cos\gamma-\cos\gamma_0) = l\lambda
\end{array}\right\}$$

Laue Equations!

a,b,c**—lattice parameter**

$\alpha_0,\beta_0,\gamma_0$—**angle between basis vectors a,b,c and S_0**

α,β,γ —**angle between basis vectors a,b,c and S**

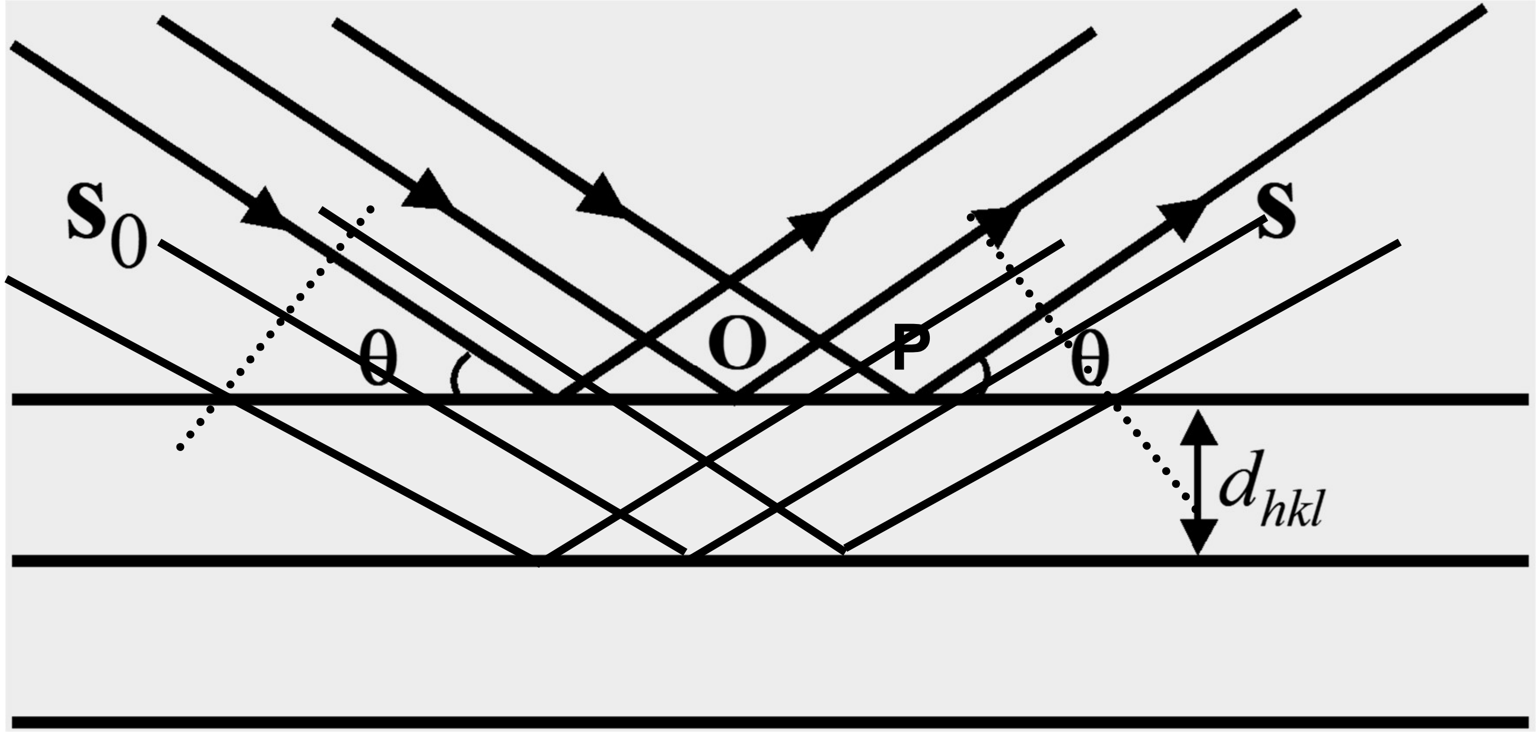
h,k,l — **indices of diffraction, integers**

which may not be prime to each other and are different from Miller indices for crystal plane!

- **Each equation defines a cone of diffraction.**
- **Only when the three cones of diffraction intersect can the diffraction beam be observable!**

2. The Bragg’s Law

Bragg considered the diffraction arising from reflection by lattice planes.



Conditions to obtain constructive inferences,

a. The scattered x-ray must be coplanar with the incident x-ray and the normal of the lattice plane.

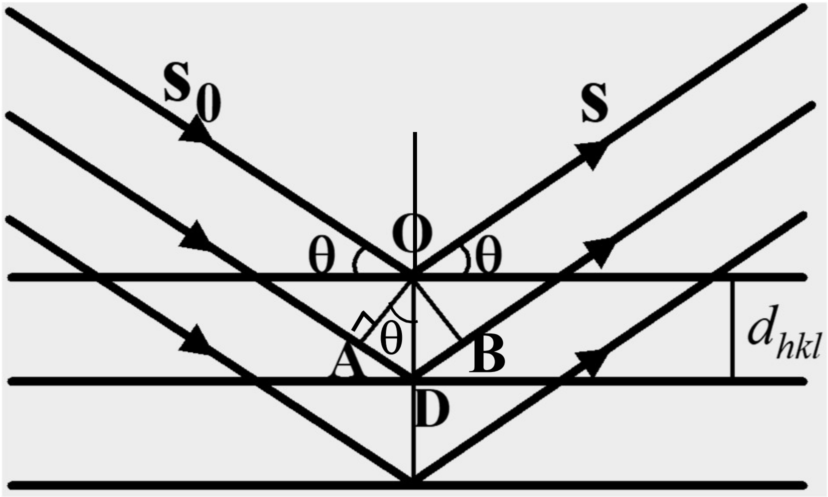
b. $\theta_S = \theta_{S0}$

The difference in path lengths,

$\Delta = \mathrm{AD} + \mathrm{DB} = 2d_{(hkl)}\sin\theta$

Condition for diffraction:

$\Delta = n\lambda = 2d_{(hkl)}\sin\theta_n \quad (n=1,2,3, \dots)$



θ_n: **the angle of reflection**

n: **the order of the reflection**

Define $\mathbf{d}_{nhnknl} = \mathbf{d}_{(hkl)}/\mathbf{n}$ → $2\cdot d_{nhnknl}\cdot\sin\theta_{nh,nk,nl} = \lambda$

miller indices

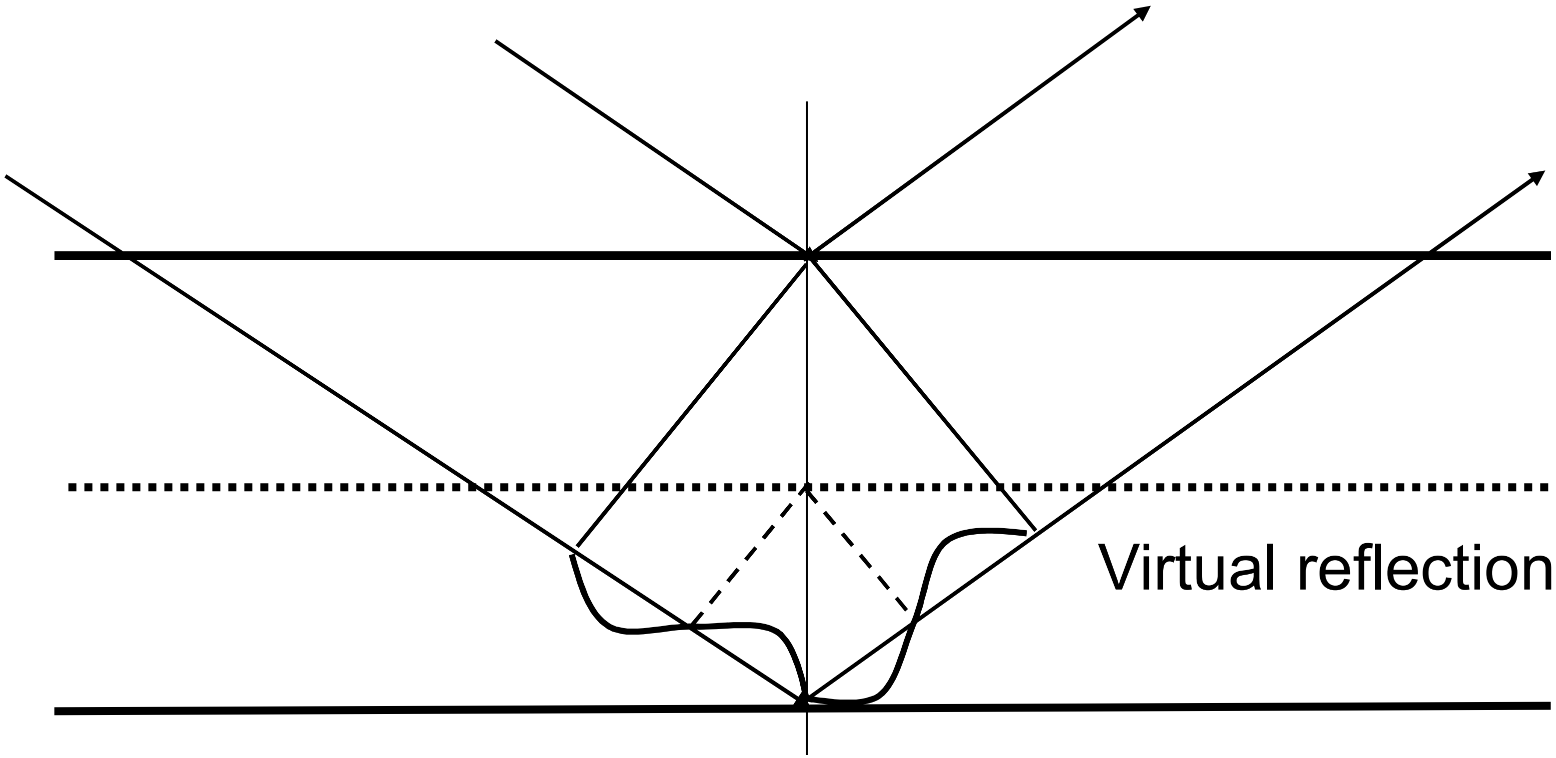
Note: n is not measurable! Let $\mathbf{d}_{nhnknl} = \mathbf{d}_{hkl}$

reflection indices

Bragg's Law: $\mathbf{2d_{hkl}\cdot\sin\theta = \lambda}$

What is the physical meaning of d_{hkl}?

The Braggs, father and son, shared the 1915 Nobel Prize in Physics for their work in crystallography.



n=2

Virtual reflection plane

$$2d_{(hkl)} \sin\theta_n = n\lambda \quad (n=1, 2, 3, \ldots)$$

Lattice plane indices

$$2d_{hkl} \cdot \sin\theta = \lambda \qquad (d_{nhnknl} = d_{hkl}/n)$$

Diffraction indices or virtual reflection plane indices.

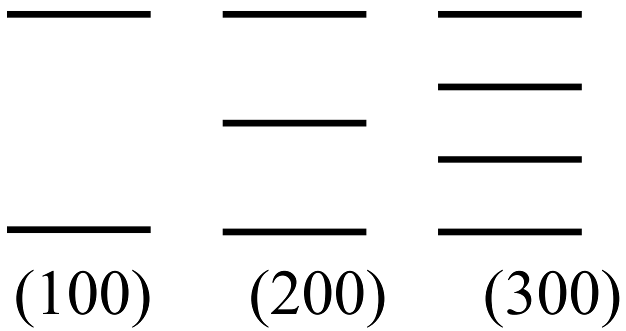
The Bragg's law defines the direction of diffraction beams from a given set of lattice planes!

diffraction crystal planes -

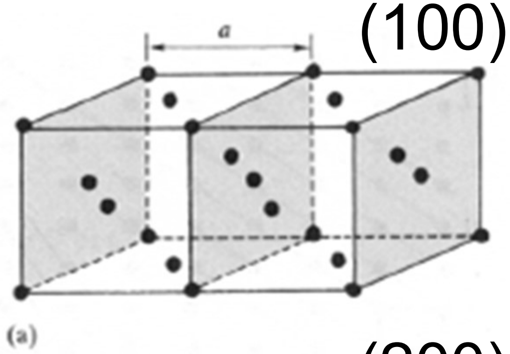
(100), (200), …

Families of planes

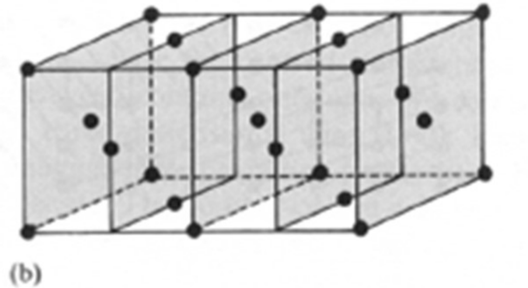
Lattice planes-(100)



(100)



(200)



The Bragg's Law vs. Laue equation:

- Both equations define the relationship between the direction of diffraction beams, the x-ray wavelength and the parameters of a crystal lattice.
- **The Bragg's law**: simple, easier to derive ***lattice parameters*** from the *direction of diffraction beams*. $2d_{hkl} \cdot \sin\theta = \lambda$

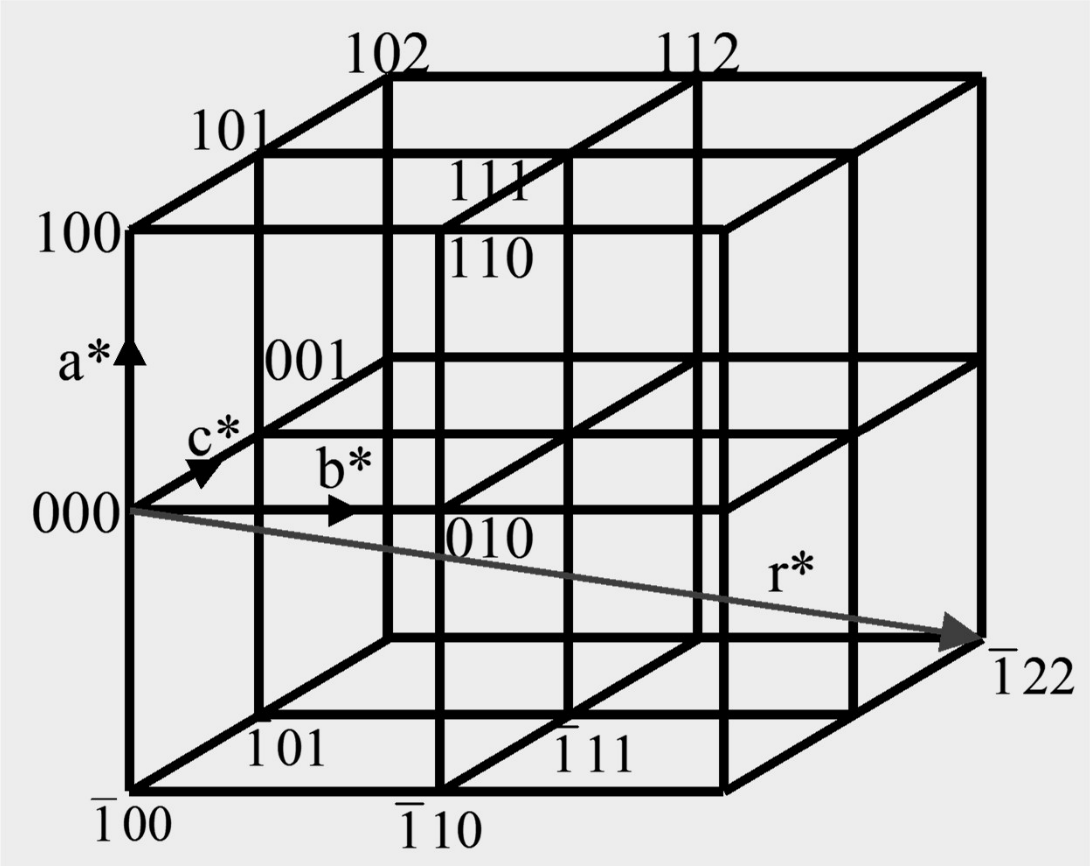
3. Reciprocal lattice

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

Basis vectors of a reciprocal lattice

$$\vec{r}^* = h\vec{a}^* + k\vec{b}^* + l\vec{c}^*$$

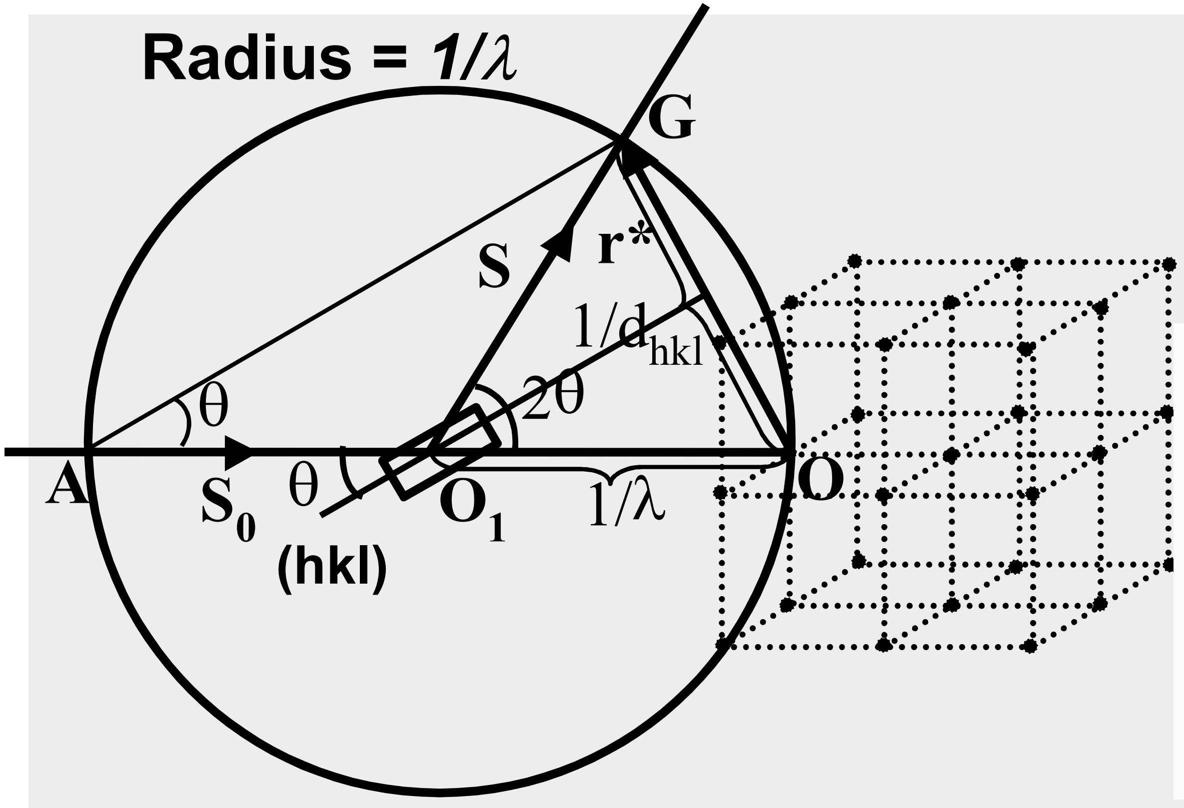
$$\left|\vec{r}^*\right| = 1/d_{hkl}$$



A reciprocal lattice point corresponds to a diffraction (lattice) plane of its original lattice!!!!!!!!!!!!

A reciprocal vector r* is perpendicular to a lattice plane with the same indices (hkl).

4. Ewald sphere (reflection sphere)



G: a diffraction point
/a reciprocal lattice point

Only when the reciprocal lattice point is located on the Ewald sphere can constructive interference occur !

$$|OG| = 2|O_1O^*|\sin\theta = (2/\lambda)\sin\theta = 1/d_{hkl} \qquad \because 2d_{hkl}\sin\theta = \lambda$$

- **Monochromic x-ray → fixed radius of the Ewald sphere!**
- **Fixed single crystal → Very few diffraction data!**

How to get more diffraction data?

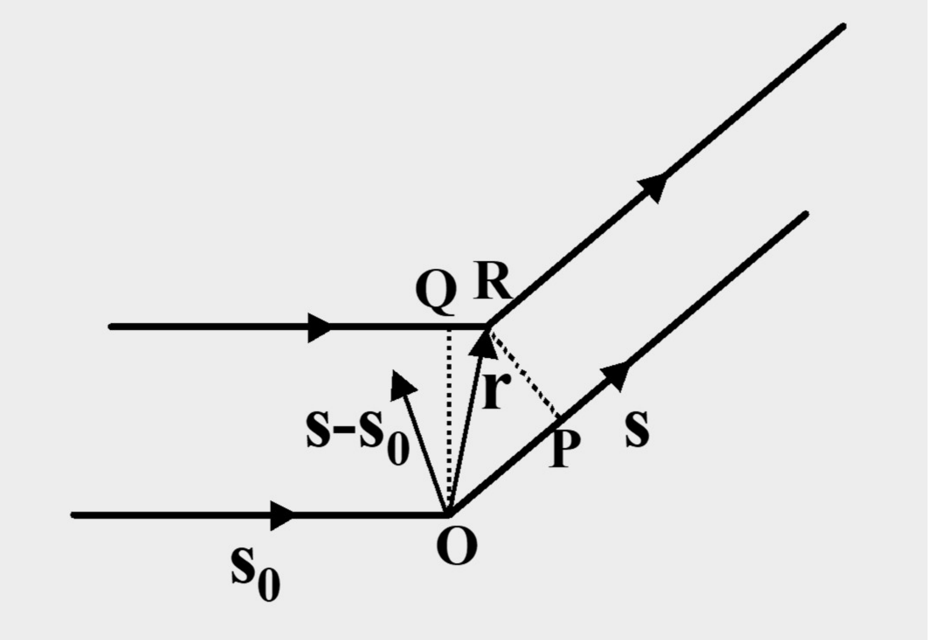
a) Fixed λ: Rotate the crystal to enable more reciprocal points (diffractions) dynamically located on the Ewald sphere.

b) Fixed crystal: use x-rays with varying wavelengths (e.g., white x-ray). By doing so, the Ewald sphere becomes filled.

- The first technique is preferred and has been widely used in practice!
- The second method can be used to determine the orientation of a single crystal.

7.3.3. The intensity of diffraction beam

1. The principle of X-ray scattering



To save your time,
Let's neglect part 1 and
move directly to part 2!
If you are interested in
this part, just go
through it by yourself.

For elastic scattering, each electron scatters the plane wave causing a spherical wave ($\exp[2\pi i(k\cdot r)]$).

The phase difference is: $\Delta=(\mathbf{r}\cdot\mathbf{s} - \mathbf{r}\cdot\mathbf{s}_o)/\lambda$

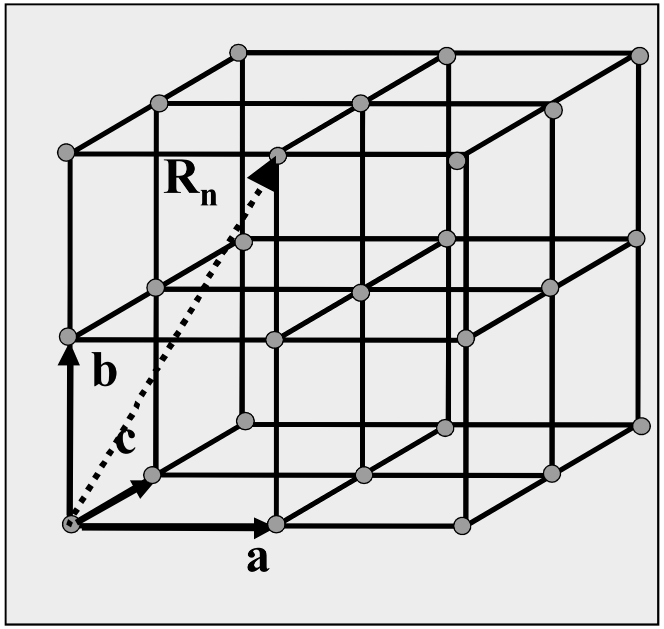
The scattered x-ray: $\exp\{2\pi i[r\cdot(s-s_0)/\lambda]\}$ or $\exp\{2\pi i[r\cdot q/\lambda]\}$

The contribution of the scattering of all electrons of a given atom:

$$\int \rho(r)\exp(2\pi i q\cdot r/\lambda)d^3r$$

For the crystal structure：

$$\rho(r)=\sum_n \rho_{cell}(r+R_n)$$



$$A=\sum_n\int \rho_{cell}(r+R_n)\exp(2\pi i q\cdot r/\lambda)d^3r$$

$$A=\left(\int \rho_{cell}(r)\exp(2\pi i q\cdot r/\lambda)d^3r\right)\sum_n \exp(2\pi i q\cdot R_n/\lambda)$$

$$=F(q)\sum_n \exp(2\pi i q\cdot R_n/\lambda)$$

F(q) --- structure factor

$$F(q)=\int \rho_{cell}(r)\exp(2\pi i q\cdot r/\lambda)d^3r$$

Supposed that there are N_1，N_2，N_3 periods along **a**，**b**，**c**, and all the atoms locate on the position of lattice points, *F(q) can be replace with a constant ‘f’. f is scattering factor of atoms.*

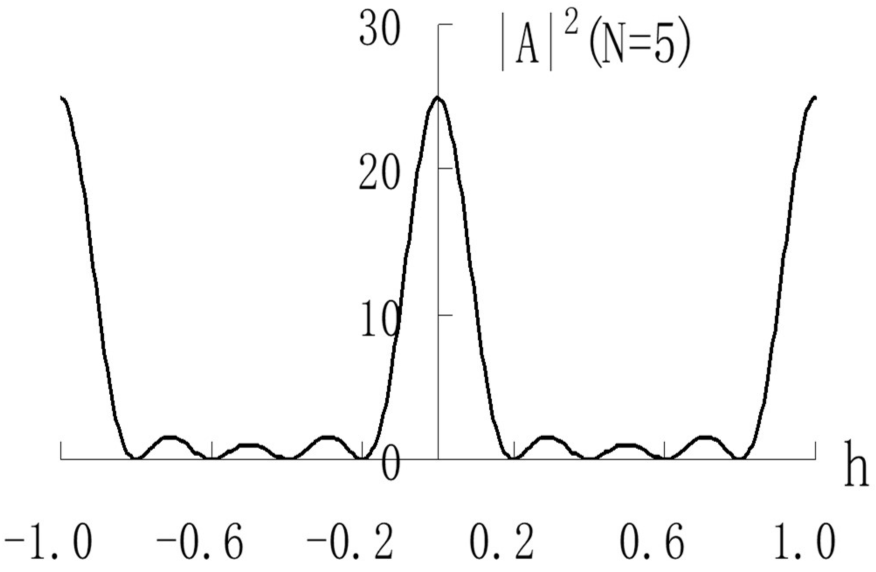
$$A_{mnp} = f\sum_{n_1=0}^{N_1-1}\sum_{n_2=0}^{N_2-1}\sum_{n_3=0}^{N_3-1} e^{2\pi i/\lambda(n_1\mathbf{a}+n_2\mathbf{b}+n_3\mathbf{c})\cdot\mathbf{q}}$$

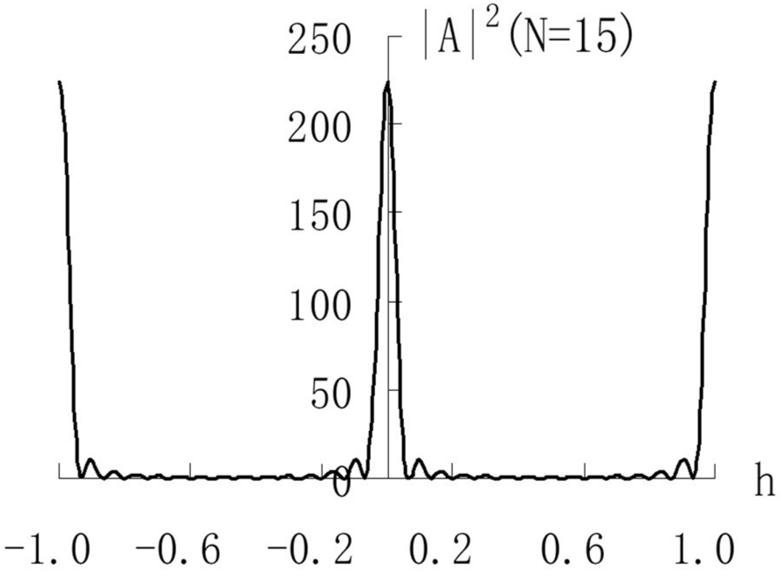
For the case of 1D and f=1,

$$A_N = \sum_{n=0}^{N-1} e^{2\pi i n\mathbf{a}\cdot q/\lambda} = \frac{1-e^{2\pi i N\mathbf{a}\cdot q/\lambda}}{1-e^{2\pi i\mathbf{a}\cdot q/\lambda}}$$

The intensity:

$$I \propto \left|A_N\right|^2 = A_N A_N^* = \frac{\sin^2\left(\frac{\pi N}{\lambda}\mathrm{a}\cdot\mathrm{q}\right)}{\sin^2\left(\frac{\pi}{\lambda}\mathrm{a}\cdot\mathrm{q}\right)} = \frac{\sin^2(\pi N h)}{\sin^2(\pi h)}$$





In the case of 3-D:

$$I \propto \lfloor A_{mnp} \rfloor^2 = |f|^2 \frac{\sin^2\left(\frac{\pi N_1}{\lambda}\mathbf{a}\cdot\mathbf{q}\right)}{\sin^2\left(\frac{\pi}{\lambda}\mathbf{a}\cdot\mathbf{q}\right)} \cdot \frac{\sin^2\left(\frac{\pi N_2}{\lambda}\mathbf{b}\cdot\mathbf{q}\right)}{\sin^2\left(\frac{\pi}{\lambda}\mathbf{b}\cdot\mathbf{q}\right)} \cdot \frac{\sin^2\left(\frac{\pi N_3}{\lambda}\mathbf{c}\cdot\mathbf{q}\right)}{\sin^2\left(\frac{\pi}{\lambda}\mathbf{c}\cdot\mathbf{q}\right)}$$

Therefore,

$\boldsymbol{a}\cdot\boldsymbol{q}/\lambda=h$，$\boldsymbol{b}\cdot\boldsymbol{q}/\lambda=k$，$\boldsymbol{c}\cdot\boldsymbol{q}/\lambda=l$ (h，k，l should be integer)

or $\boldsymbol{a}\cdot\boldsymbol{q}=h\lambda$，$\boldsymbol{b}\cdot\boldsymbol{q}=k\lambda$，$\boldsymbol{c}\cdot\boldsymbol{q}=l\lambda$

----- Laue conditions for X-ray diffraction

$$I \propto |f|^2 N_1^2 N_2^2 N_3^2 \Rightarrow \boxed{I \propto |F_{hkl}|^2 N_1^2 N_2^2 N_3^2}$$

Only those scatterings fulfilling these conditions give rise to measurable diffraction beams.

2. The intensity of diffraction beam

- The directions of the diffraction beams

Bragg's Law

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

The directions of the diffraction beams are determined by the cell parameters.

- The intensity of diffraction beam

$$I_{hkl} = K\left|F_{hkl}\right|^2$$

Structure factor

Systematic absence:
$F_{hkl} = 0 \rightarrow I_{hkl} = 0$

$$F_{hkl} = \iiint \rho(x,y,z)e^{2\pi i(hx+ky+lz)}dxdydz$$

Electron density distribution in a unit cell.

$$= \sum_{j=1}^{n} f_j e^{2\pi i(hx_j+ky_j+lz_j)}$$

Phase difference between the scattered and incident x-ray over atom j.

Sum over all atoms within a unit cell.

***f*$_j$:** atomic scattering factor defined by atomic electron density distribution.

- The intensities of the diffraction beams are determined by types of atoms and the arrangement of atoms in the cell!
- By measuring the cell parameters and the intensities of diffraction points, the atomic arrangement can be derived.

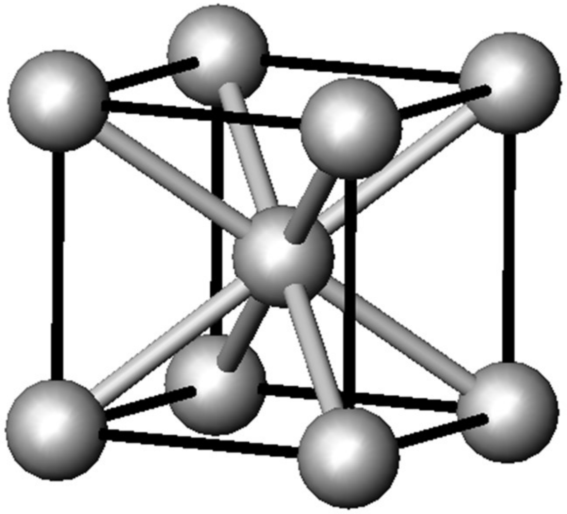
3. systematic absence

Calculation of structure factor

Example A, Body-centered crystal

Simple case: Each lattice point is a metal atom.

(e.g., Na)



$$F_{hkl} = \sum_{j=1}^{N} f_j e^{2\pi i(hx_j + ky_j + lz_j)}$$

***N* = 2**

(0,0,0)

(1/2,1/2,1/2)

$$= f_1 e^{2\pi i(h0+k0+l0)} + f_2\, e^{2\pi i(h\frac{1}{2}+k\frac{1}{2}+l\frac{1}{2})}$$

$$= f_{\mathrm{Na}}(1 + e^{\pi i(h+k+l)})$$

$(f_1 = f_2 = f_{Na})$

i) While $h+k+l = 2n+1$, $e^{\pi i(h+k+l)} = e^{(2n+1)\pi i} = -1$

→ $F_{hkl} = 0$, **Systematic absence !**

ii) While $h+k+l = 2n$, $e^{\pi i(h+k+l)} = 1 \Rightarrow F_{hkl} = 2 f_{\mathrm{Na}}$ **Strongest!**

Body-centered crystal –Two lattice point in a unit cell!
General case: each lattice point contains ***m*** different atoms.

- The total number of atoms within a unit cell is ***2m***;
- For jth atom in a structural motif (a lattice point): $(\mathbf{x_j,y_j,z_j})$
- Its body-centered equivalent: $(\mathbf{0.5+x_j,\ 0.5+y_j,\ 0.5+z_j})$

$$F_{hkl}=\sum_{i=1}^{2m} f_i e^{2\pi i(hx_i+ky_i+lz_i)}$$

$$=\sum_{j=1}^{m}\{f_j e^{2\pi i(hx_j+ky_j+lz_j)}+f_j\,e^{2\pi i[h(\frac{1}{2}+x_j)+k(\frac{1}{2}+y_j)+l(\frac{1}{2}+z_j)]}\}$$

$$=[1+e^{\pi i(h+k+l)}]\sum_{j=1}^{m} f_j e^{2\pi i(hx_j+ky_j+lz_j)}$$

While $h+k+l=2n+1$,

$$e^{\pi i(h+k+l)}=e^{(2n+1)\pi i}=-1\Rightarrow F_{hkl}=0$$

Systematic absence

Face-centered cubic crystal – general case

- Lattice points (LPs): (0,0,0), (1/2,1/2,0)+, (0,1/2,1/2)+, (1/2,0,1/2)+
- Each lattice point contains ***m*** atoms, $\{(x_j,y_j,z_j)\}$ (j=*1,…,**m***)
- Each unit cell contains N=***4m*** atoms, e.g., an atom $A(x_i,y_i,z_i)$ in one LP has other three equivalent ***A*** atoms within the same unit cell!

$$F_{hkl} = \sum_{i=1}^{N=4m} f_i e^{2\pi i(hx_i+ky_i+lz_i)}$$

Sum up over all atoms within a unit cell!

$$\mathrm{F_{hkl}} = [1+e^{2\pi i(\frac{h}{2}+\frac{k}{2})}+e^{2\pi i(\frac{h}{2}+\frac{l}{2})}+e^{2\pi i(\frac{k}{2}+\frac{l}{2})}]\times\sum_{j=1}^{m} f_j e^{2\pi i(hx_j+ky_j+lz_j)}$$

From translation symmetry of fcc!

sum up over all atoms within a LP!

When *h,k,l* are neither all even nor all odd, $F_{hkl} = 0$, ***systematic absence!***

When *h,k,l* are all even or all odd, **diffraction observable**!

$$\mathrm{F_{hkl}} = 4\sum_{j=1}^{n} f_j e^{2\pi i(hx_j+ky_j+lz_j)}$$

Example. Unit cell has a 2_1 screw axis along the *c* axis.

→ **Equivalent positions: (x, y, z), (-x , -y , z+1/2)**

$$F_{hkl} = \sum_{j=1}^{N} f_j \{ exp[i2\pi(hx_j + ky_j + lz_j)] + exp[i2\pi(-hx_j - ky_j + l(z_j + \frac{1}{2}))] \}$$

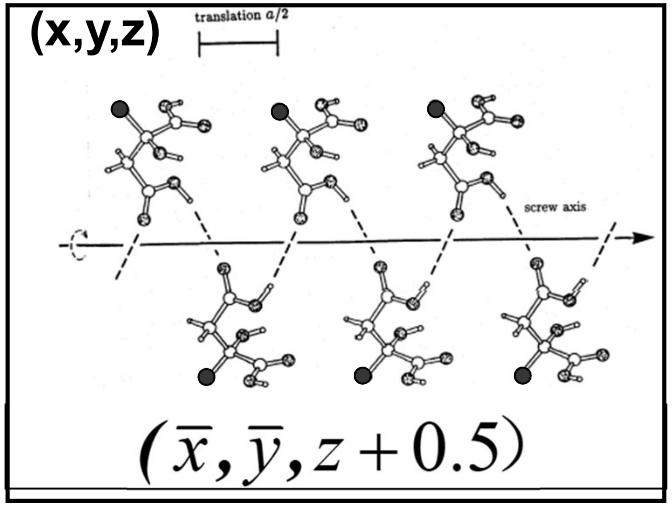
$$F_{00l} = [(1 + exp(i\pi l))] \sum_{j=1}^{N} f_j \, exp(i2\pi l z_j)$$

Sum over all atoms of a molecule.

l = 2n+1 $F_{00l} = 0$

systematic absence

Each molecule has N atoms.



Herein two molecules within a unit cell are correlated by 2_1 axis.

How about systematic absence arising from such screw axes as 3_1, 4_1 and 6_1 ?

- ***3_1||c-axis***

$$F_{00l}=[1+\boldsymbol{exp}(\frac{2\pi li}{3})+\boldsymbol{exp}(\frac{4\pi li}{3})]\cdot\sum_{i=1}^{N/3}\boldsymbol{exp}(i2\pi lz_i)$$

$$=[1+2\boldsymbol{cos}(\pi l)\boldsymbol{cos}(\frac{\pi l}{3})]\sum_{i=1}^{N/3}\boldsymbol{exp}(i2\pi lz_i)$$

→ Systematic absence when $l \neq 3$m (m=1,2,…)!

- ***n_1 //c-axis***

$$F_{00l}=\sum_{j=1}^{n}\exp(\frac{2\pi(j-1)li}{n})\bullet\sum_{i=1}^{N/n}\exp(i2\pi lz_i)$$

→ Systematic absence when $l \neq m\cdot n$ (m=1,2,…)!

Systematic Absence

- **Crystals of the same lattice type behave similarly in systematic absence!**
- **Crystal structures which contain centering, glide plane and screw axis will have systematic absences.**
- **Namely, some reflections/diffractions will be systematically absent in such a crystal lattice that has centering, glide plane or screw axis.**

Systematic Absence and Symmetry (p214-215)

Types of reflection	Conditions for extinction (systematic absence)	Cause of extinction	Centering and symmetry elements
hkl	$h+k+l$ = odd	I-centred	I
	$h+k$ = odd	C-centred	C
	$h+l$ = odd	B-centred	B
	$k+l$ = odd	A-centred	A
	h,k,l not all even and not all odd	Face-centred	F
	$-h+k+l$ not multiples of 3	R-centred	R(hexagonal)
$0kl$ (or $h0l$, $hk0$)	k =odd	Translation in (100) b/2	b-glide ⊥a (b,c)
	l =odd	c/2	c-glide⊥a (b,c)
	$k+l$ =odd	(100) glide (b+c)/2	n-glide⊥a (b,c)
	$k+l$ not multiples of 4	planes (b+c)/4	d-glide⊥a (b,c)
$00l$ (or $h00$, or $0k0$)	l =odd	Translation c/2	2_1, 4_2, 6_3
	l not multiples of 3	Along c/3	3_1, 3_2, 6_2, 6_4
	l not multiples of 4	(001) c/4	4_1, 4_3
	l not multiples of 6	Screw axis c/6	6_1, 6_5

7.3.4 Applications of X-ray diffraction

1. Methods

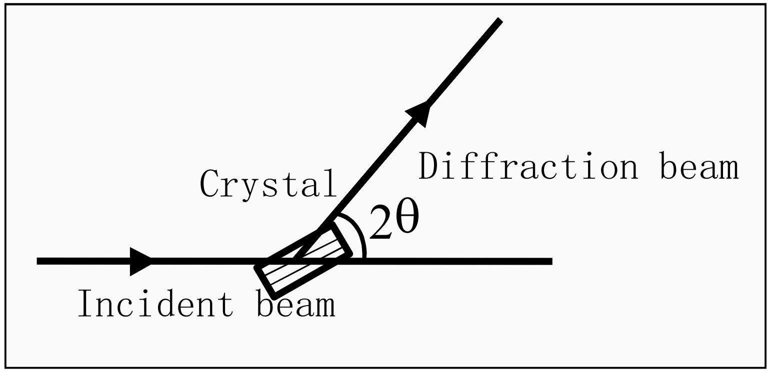
* Single crystal diffraction

Monochromatic camera method -- Monochromatic X-ray

Rotation, Oscillation, Weissenberg …

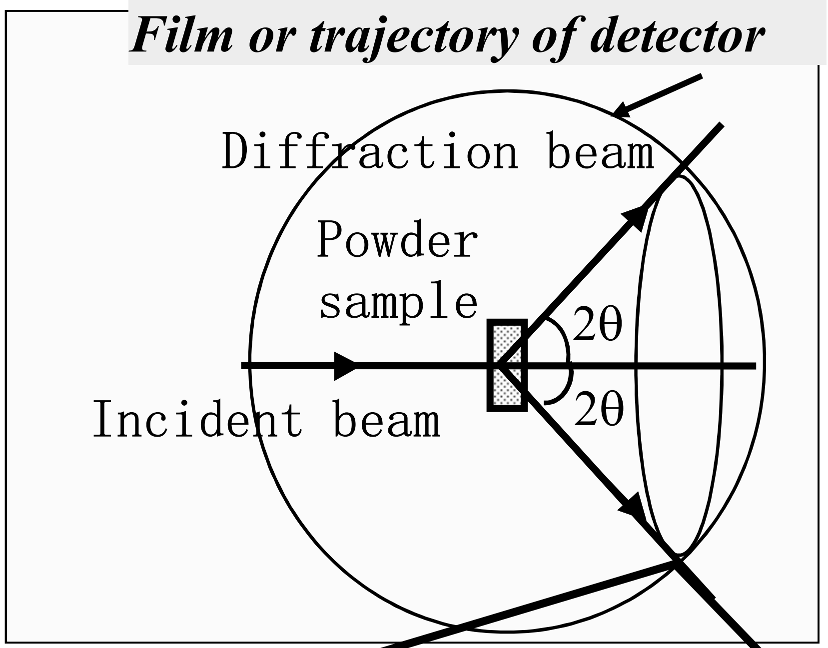
Laue photography --- white X-ray

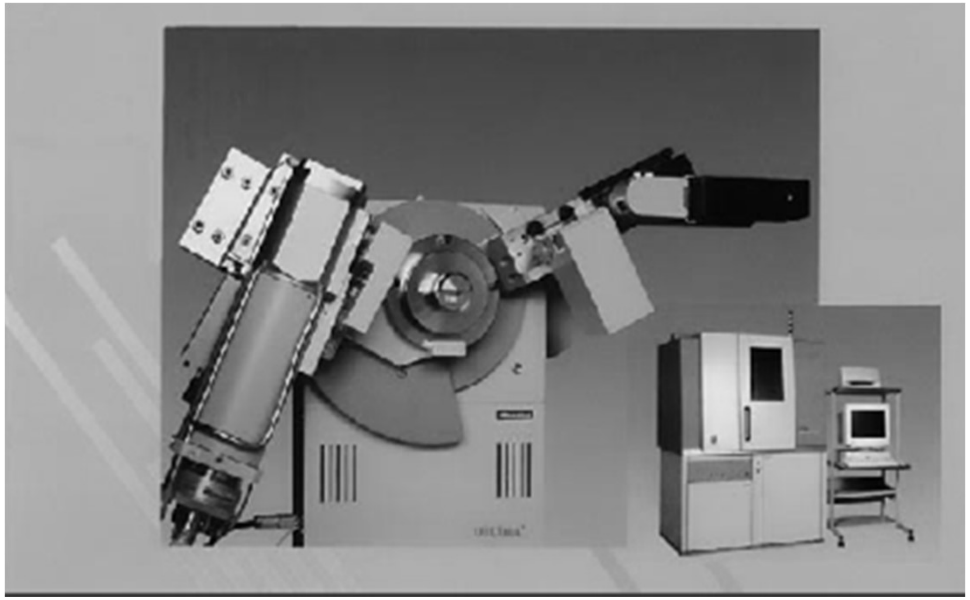
Diffractometer -- Monochromatic X-ray



* Powder diffraction

Monochromatic X-ray





Powder Diffractometer

- **In a powder sample, the microcrystalls orient differently, so does a given lattice plane in the sample.**
- **Thus a given lattice plane gives a cone of diffraction beam with an specific angle 2θ. (Why?)**

Radiation sources

X-ray tubes

Synchrotron radiation

Monochromator – e.g.HOPG

Filter – e.g. Ni for Cu Kα

Detectors

- Film

  - poor sensitivity, high background, low dynamic range

- Scintillation counters

  - good sensitivity, low background, high dynamic range

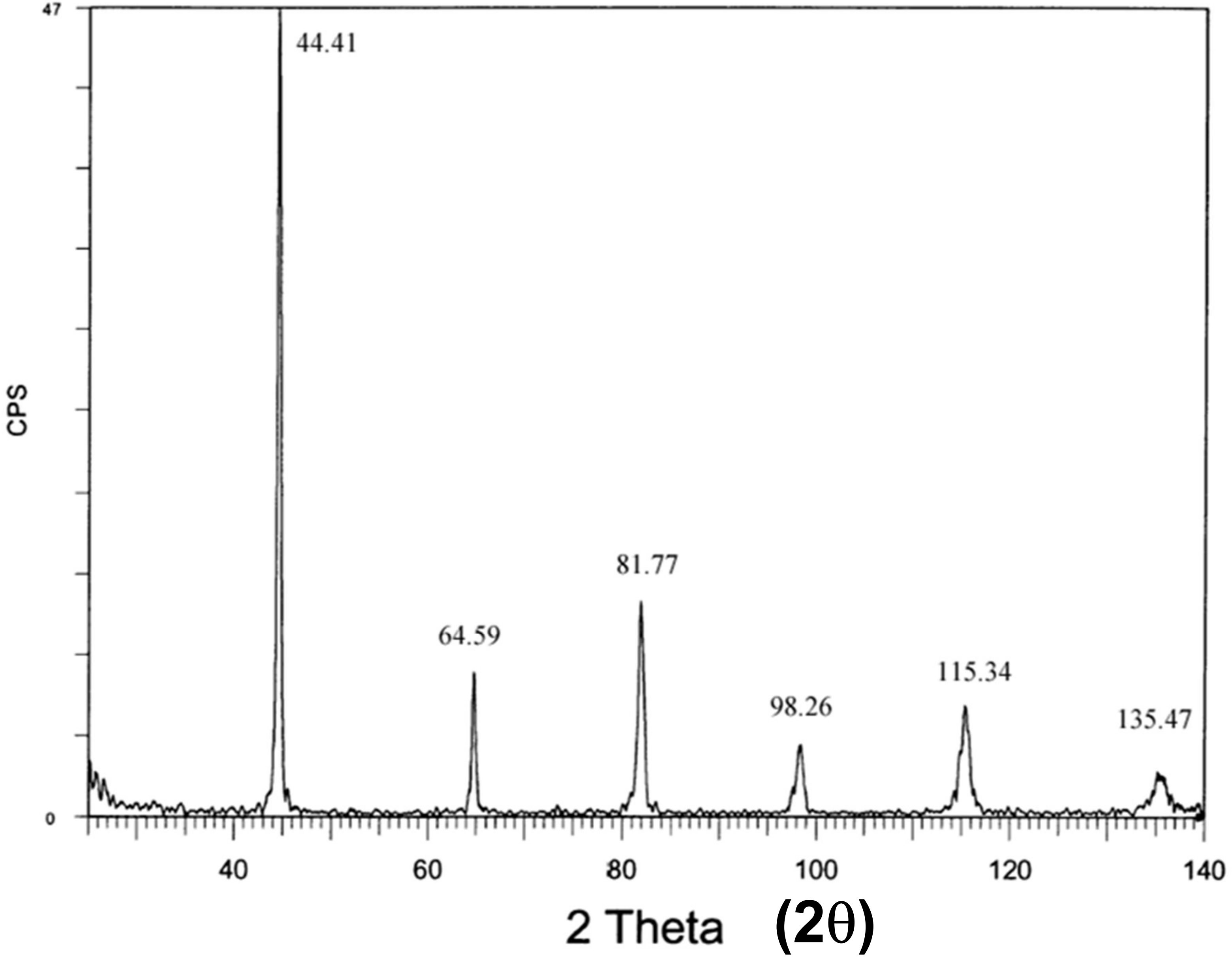
- Imaging plates

  - good sensitivity, low background, good dynamic range, very efficient data collection

- CCDs and Multiwire detectors (widely used nowadays)

  - fast readout, good sensitivity, low background, good dynamic range, very efficient data collection

Automated diffractometer method



2. Applications of X-ray diffraction

a. crystal structure determination

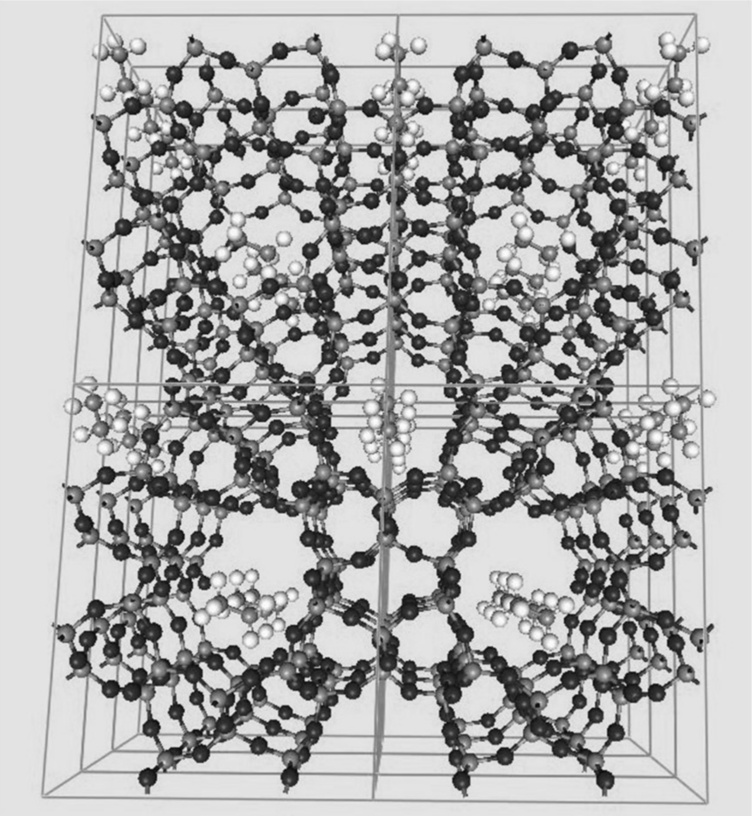
Direction & intensity data collection

Indexing → **Crystal system and Cell parameters**

$$I_{hkl} = K\left|F_{hkl}\right|^2$$

Phase problem

$$F(hkl) = \iiint \rho(x,y,z)\, e^{2\pi i(hx+ky+lz)}\, dx\,dy\,dz$$



Inverse Fourier Transform

$$\rho(x,y,z) = V^{-1}\sum_h \sum_k \sum_l F(hkl)\, e^{-2\pi i(hx+ky+lz)}$$

$$\sum A_i(x,y,z)$$

Example: Indexing of a cubic system

$d_{hkl} = a/\sqrt{h^2+k^2+l^2}$ $\boxed{2d_{hkl}\sin\theta = \lambda}$ **Bragg's law**

$\sin^2\theta = (\lambda/2a)^2(h^2+k^2+l^2)$

$$\sin^2\theta \propto h^2+k^2+l^2 \Rightarrow \boxed{\sin^2\theta_1 : \sin^2\theta_2 : \sin^2\theta_3 : \sin^2\theta_4 : \ldots}$$

General steps of indexing:

1. **Get the directions of the diffraction beams, $\{\theta_i\}$**
2. **Get** $\boxed{\sin^2\theta_1 : \sin^2\theta_2 : \sin^2\theta_3 : \sin^2\theta_4 : \ldots}$
3. **Get** $(h^2+k^2+l^2)_1 : (h^2+k^2+l^2)_2 : (h^2+k^2+l^2)_3 \ldots.$
4. **Get the lattice type and cell parameters.**

Indexing of a cubic system

$$\sin^2\theta = (\lambda/2a)^2(h^2+k^2+l^2) \Rightarrow \sin^2\theta \propto h^2+k^2+l^2$$

$$\Rightarrow \sin^2\theta_1 : \sin^2\theta_2 : \sin^2\theta_3 : \sin^2\theta_4 : \ldots$$

$$= (h^2+k^2+l^2)_1 : (h^2+k^2+l^2)_2 : (h^2+k^2+l^2)_3 \ldots.$$

Characteristic line sequences of cubic systems:

P: (*hkl*) 100, 110, 111, 200, 210, 211, 220, 221, 222, 300, ….

（**$h^2+k^2+l^2$**） 1, 2, 3, 4, 5, 6, 8, 9, 10, 11, 12, 13, …

Systematic absence

I: (*hkl*) *100*, 110, *111*, 200, *210*, 211, 220, *221*, 222, *300,* …

（**$h^2+k^2+l^2$**） 2, 4, 6, 8, 10, 12, 14, 16 … →(1: 2: 3: 4: 5: 6: 7: 8:…)

***F*: (*hkl*)** *100, 110,* 111, 200, *210, 211,* 220, *221, 300,* 311, 222, ….

（**$h^2+k^2+l^2$**） 3, 4, 8, 11, 12, 16, 19, 20 …

Example for the indexing of cubic system and its applications

Sample: NaCl   Condition: Cu Kα, λ=1.5418 Å, R = 50 mm

(1) Measure sample and relative intensity

(2) Calculate the position of diffraction lines (usually 2θ in Ewald sphere)

(3) Calculate θ

(4) Calculate $\sin^2\theta$

(5) Calculate $\sin^2\theta_1 : \sin^2\theta_2 : \sin^2\theta_3 : \sin^2\theta_4 : \ldots = 3:4:8:11:12:\ldots$

(6) Identify Bravais lattice → face-centered cubic

(7) Indexing and calculate $h^2+k^2+l^2$, calculate d_{hkl} and a.

FCC: ***(hkl)*** *100, 110,* 111, 200, *210, 211,* 220, *221, 300,* 311,222, ….

（$h^2+k^2+l^2$） 3, 4, 8, 11, 12, 16, 19, 20 …

(7) Index and calculate $h^2+k^2+l^2$

No.	I	2 θ	θ	$\sin^2\theta$	$h^2+k^2+l^2$	hkl
1	W	27.46	13.73	0.05631	3	111
2	S	31.80	15.90	0.07508	4	200
3	S	45.60	22.80	0.15016	8	220
4	W	54.06	27.03	0.20647	11	311
5	S	57.50	28.75	0.22524	12	222
6	S	66.44	33.22	0.30032	16	400
7	W	73.30	36.65	0.35663	19	331
8	S	77.56	38.78	0.37540	20	420
9	S	84.30	42.15	0.45045	24	422

Measured in Ewald sphere by x-ray diffraction

FCC

Indexing

(8) Calculate lattice parameter

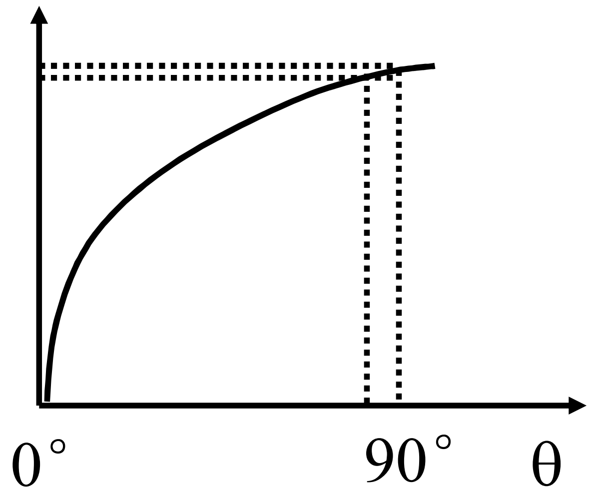
$$sin^2\theta = \frac{1.5418^2}{4a^2} \times (h^2 + k^2 + l^2)$$

$$\therefore a = \frac{1.5418}{2\,sin\theta} \times \sqrt{h^2 + k^2 + l^2}$$

Least-square method, plot method, or *high angle values*,…

a=5.628 Å

Why do we use high angle values?



$$\mathbf{d_{hkl} = \lambda/(2sin\theta)}$$

(9) ρ= 2.165 g/cm³ for NaCl

$$n = \frac{\rho V}{M/N_0} = \frac{2.165 \times (5.628 \times 10^{-8})^3}{[(23 + 35.5)/6.022 \times 10^{23}]} = 4$$

One unit cell contains 4 NaCl

(i.e., each lattice point contains a NaCl.)

Example B. (x-ray λ=1.5418 Å)

Line	2θ	θ	$\sin^2\theta$	$\sin^2\theta_i / \sin^2\theta_1$	$h^2+k^2+l^2$	hkl
1	40.26	20.13	0.1184	1	2	110
2	58.26	29.13	0.2370	2	4	200
3	73.20	36.60	0.3555	3	6	211
4	87.02	43.51	0.4740	4	8	220
5	100.64	50.32	0.5923	5	10	310
6	114.92	57.46	0.7109	6	12	222
7	131.16	65.58	0.8290	7	14	321
8	153.58	76.79	0.9470	8	16	400

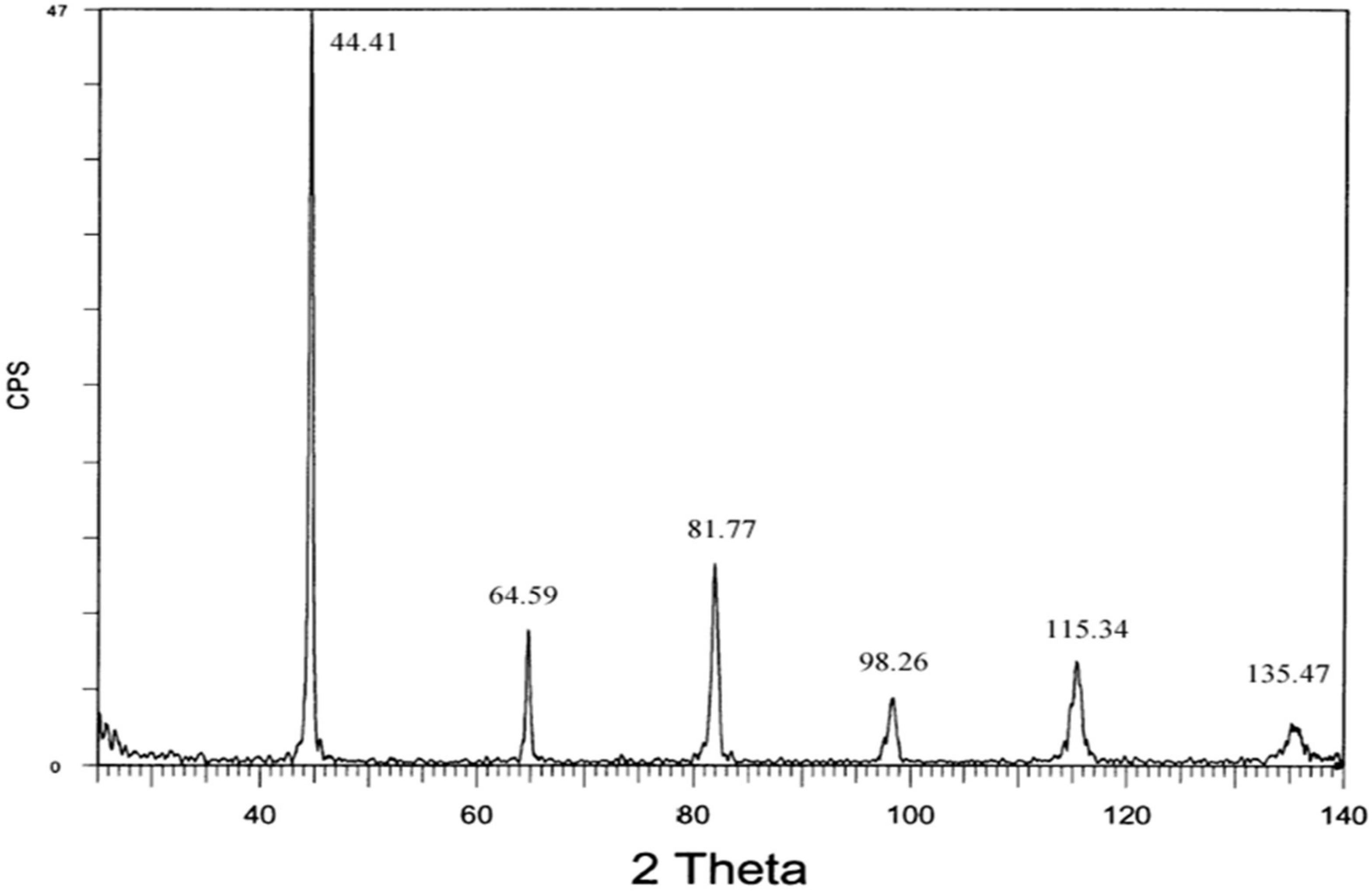
BCC

indexing

As λ=1.5418 Å,

$$a = \frac{\lambda}{2\sin\theta} \cdot \sqrt{h^2 + k^2 + l^2} = \frac{1.5418}{2\sin 76.79} \times \sqrt{4^2 + 0^2 + 0^2} = 3.16A$$

b. Applications of powder diffractions



Peak Positions Peak Intensities Peak Shapes and Widths

b. Applications of powder diffractions

Information contained in a Diffraction Pattern

Peak Positions

Crystal system, cell parameters, qualitative phase identification

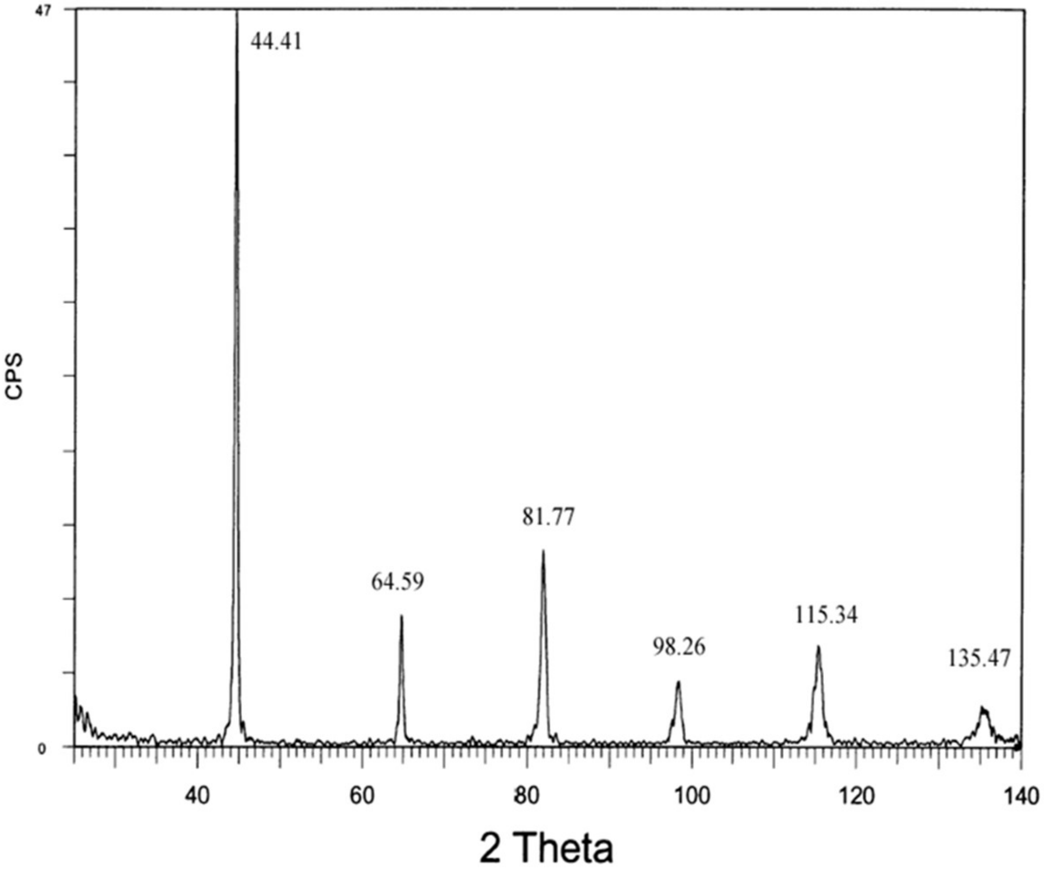
Peak Intensities

Unit cell contents, quantitative phase fractions

Peak Shapes and Widths

Crystallite size, Non-uniform microstrain

(i) Peak Positions and Intensities



- Qualitative Analysis:

  a) One crystal phase correspond to a set of diffraction peaks. (being different from the spectroscopic analysis)

  b) Phase analysis

- Quantitative Analysis:

  The peak intensities are proportional to the weight percentage of the corresponding phase.

(ii) Changes of lattice parameters－Solid solution, doping

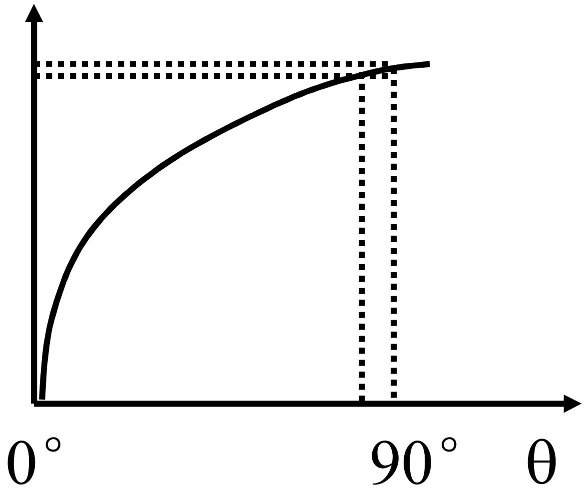
Using high-angle diffraction data or applying least square method.

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

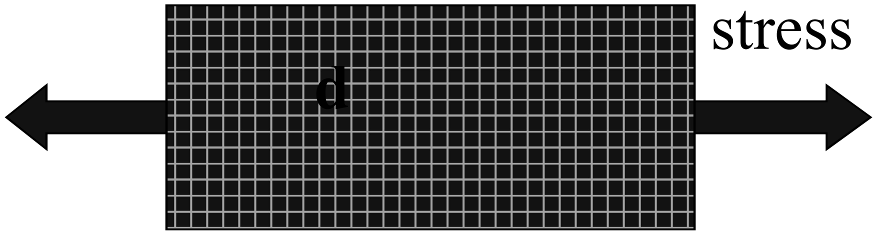
Maximal θ

→ minimal Δd/Δθ

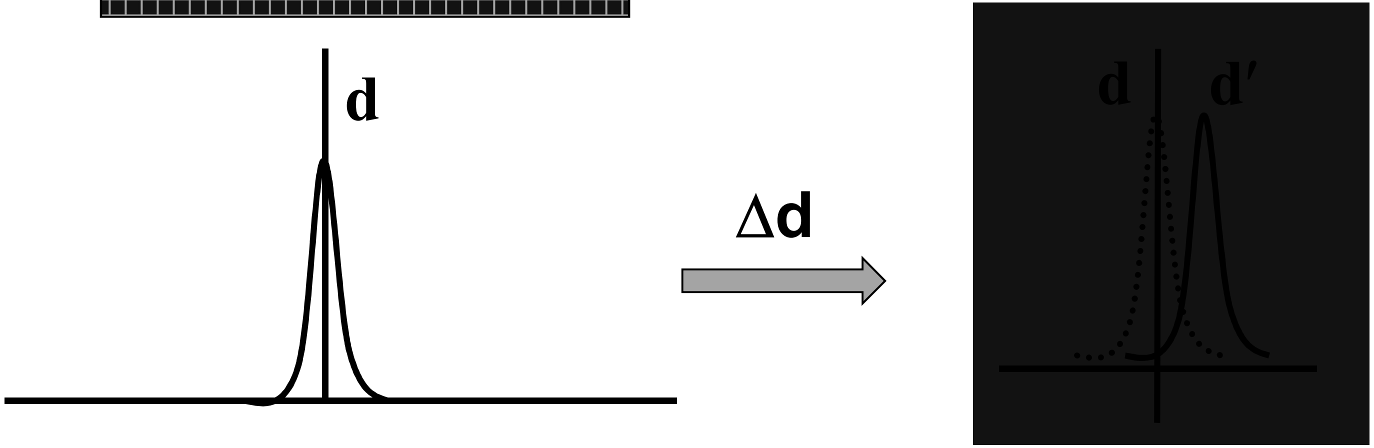
Why use high angle values?



(ii) Changes of lattice spacing along specific directions—residue stress

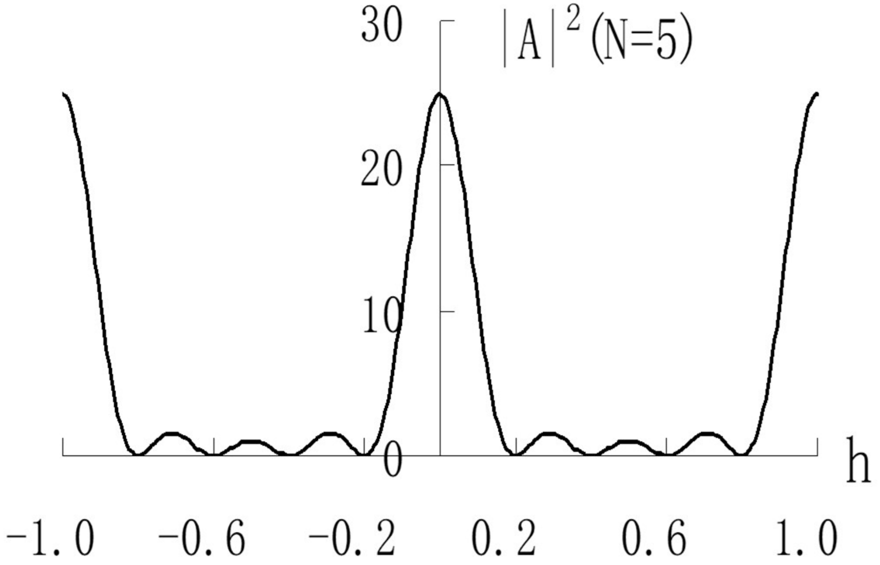


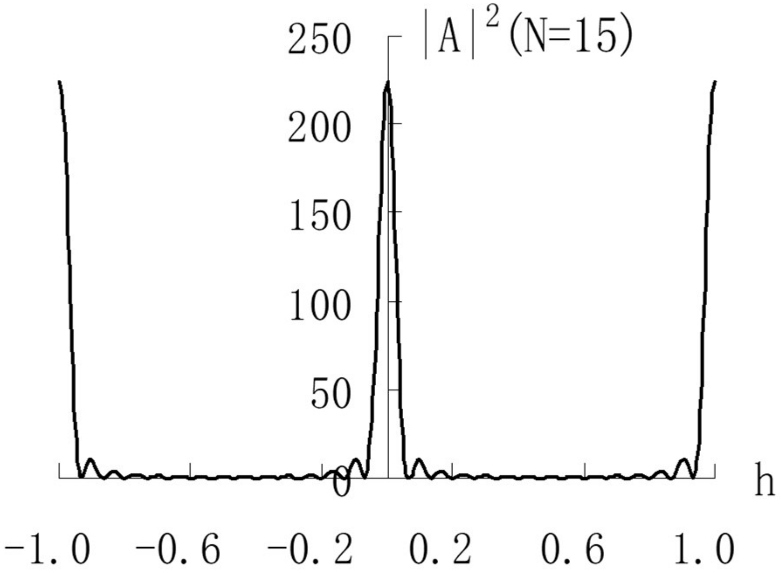
$$2d_{hkl}\sin\theta = \lambda \rightarrow$$
$$\sin\theta = \lambda/(2d_{hkl})$$



- The residue stress in a specific direction increases the corresponding d-spacing of a crystal.
- Δd is proportional to the strength of crystal strain in the direction.

(iii) The width of diffraction peaks —— Crystallite size

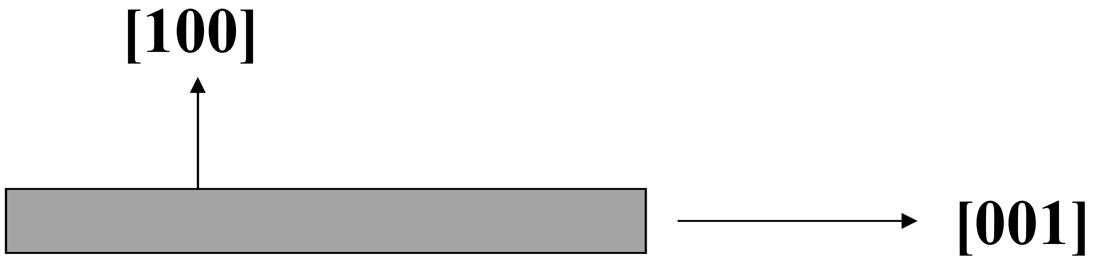




$$I \propto \left|F_{hkl}\right|^2 N_1^2 N_2^2 N_3^2 = \left|F_{hkl}\right|^2 \left|A\right|^2$$

N_1, N_2, N_3 periods along the lattice axes within a microcrystal

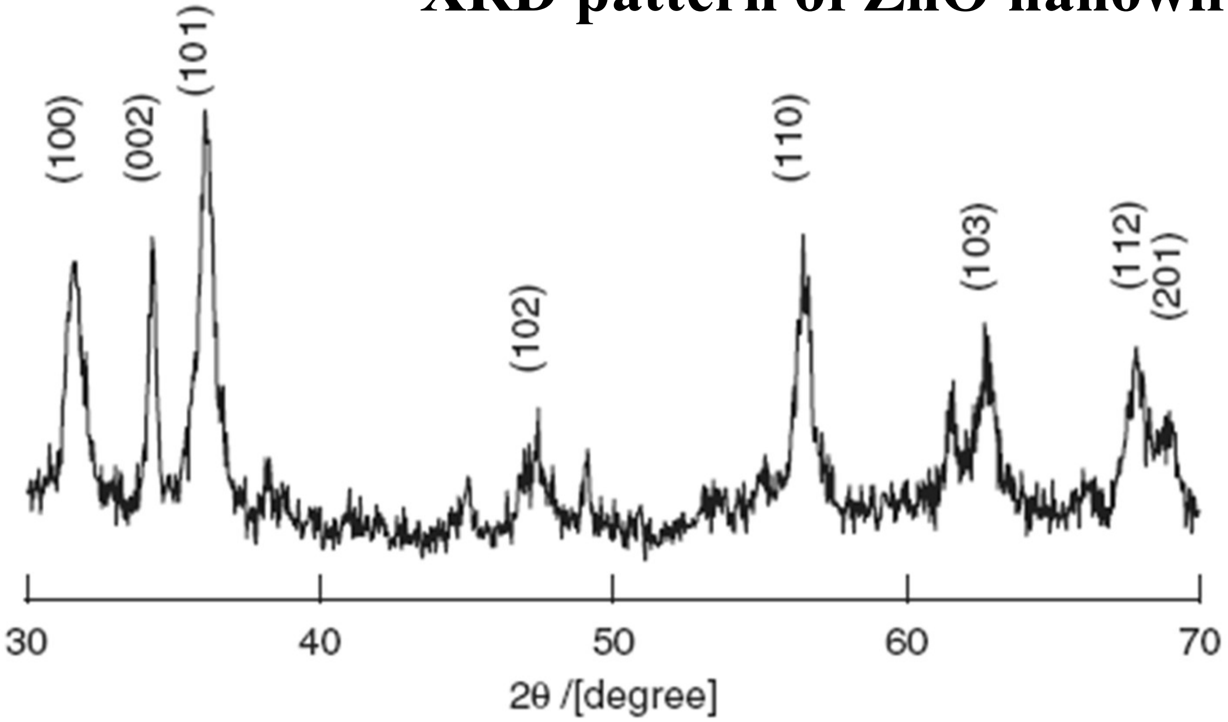
- **The smaller N in a specific** direction **[hkl], the broader of the (hkl) diffraction peak.**



[100]

[001]

XRD pattern of ZnO nanowires



The diffraction peaks arising from (100)-like planes are much more broad than those from (001)-like planes.

(iii) The width of diffraction peaks —— Crystallite size

Widely exploited in the research of nanoparticles!

Scherrer formula: (size ~1nm to 100nm)

$$D_{hkl} = \frac{K \cdot \lambda}{\beta \cdot \cos\theta} = \frac{K \cdot \lambda}{(B - B_0) \cdot \cos\theta}$$

(K =0.9 or 1.0)

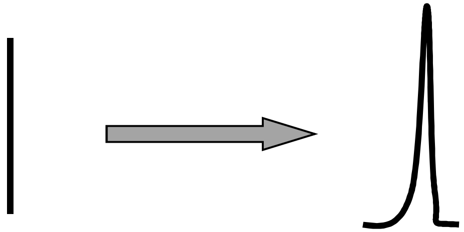
use small angle values!

Small-angle scattering – particle size

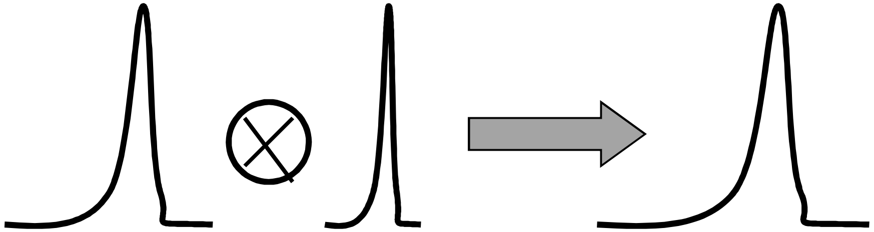
D_{hkl} average size along the direction perpendicular to (hkl) plane.

B measured peak width

B_0 Instrumental width, using standard sample (e.g. α-SiO_2 with crystallite size of 25－44μm）

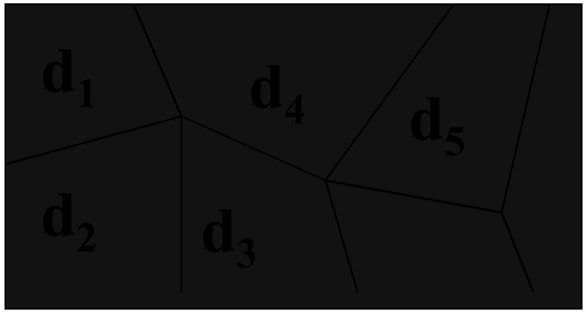


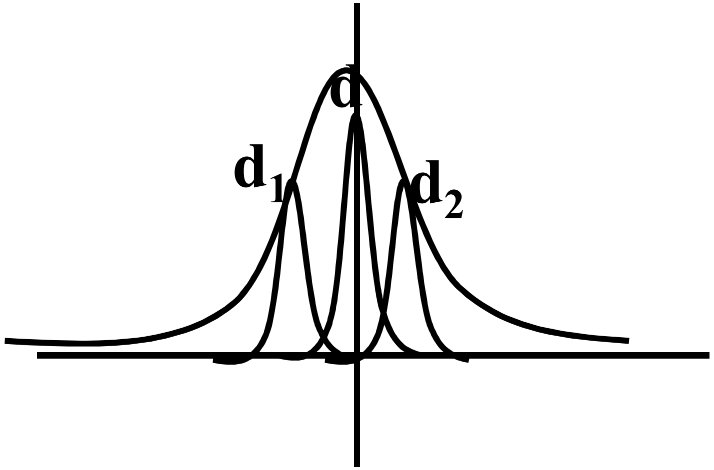
Instrumental width（B_0）



(iii) The width of diffraction peaks — Lattice Distortion

晶格的畸变（不均匀应变、微观应变、内应力）





$\eta = \Delta d / d$

$2(d+\Delta d)\sin(\theta+\Delta\theta)=\lambda$

or $2d(1+\eta)\sin(\theta+\Delta\theta)=\lambda$

η and $\Delta\theta$ are very small,

and hence ,

$2\Delta\theta = -2\eta \mathrm{tg}\theta$ or

$\beta' = 2\eta \mathrm{tg}\theta$

Separation of the effects of Crystallite size and Lattice Distortion

$$\beta = \beta_i + \beta_i^{'} = \frac{K \cdot \lambda}{D \cdot \cos\theta} + 2\eta tg\theta$$

$$\frac{\beta\cos\theta}{\lambda} = 2\eta\frac{\sin\theta}{\lambda} + \frac{K}{D}$$

Measuring two or more diffraction peaks.

(iii) The profile of diffraction peaks —— Crystallite size distribution

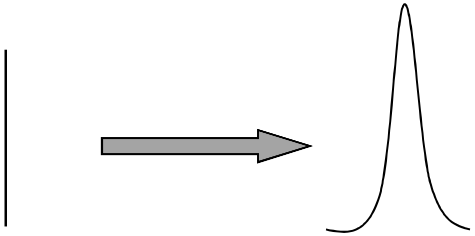
$$I \propto \left|A_N\right|^2 = A_N A_N^* = \frac{\sin^2\left(\dfrac{\pi N}{\lambda}\mathbf{a}\cdot\mathbf{S}\right)}{\sin^2\left(\dfrac{\pi}{\lambda}\mathbf{a}\cdot\mathbf{S}\right)}$$

Derived from Bragg equation

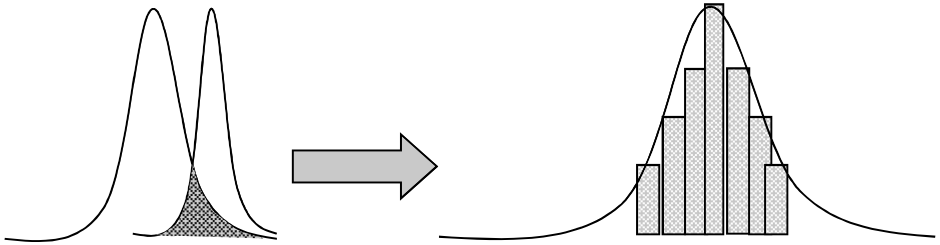
$$f_p(s) = K\sum_{n=1}^{m} P(n)\frac{\sin^2(\pi ns)}{\sin^2(\pi s)}$$

$f_p(s)$ is the line profile of diffraction peak

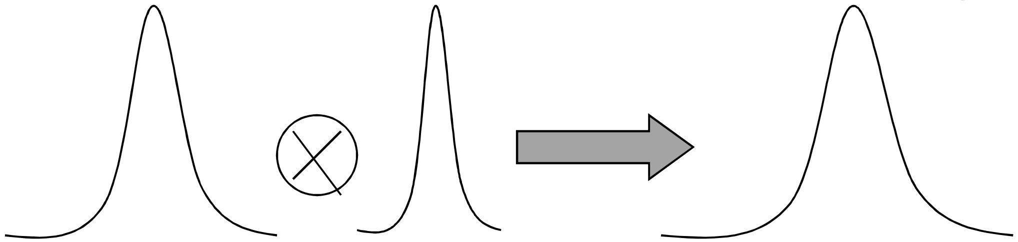
P(n) is Crystallite size distribution function



Instrumental（B_0）



Convolution

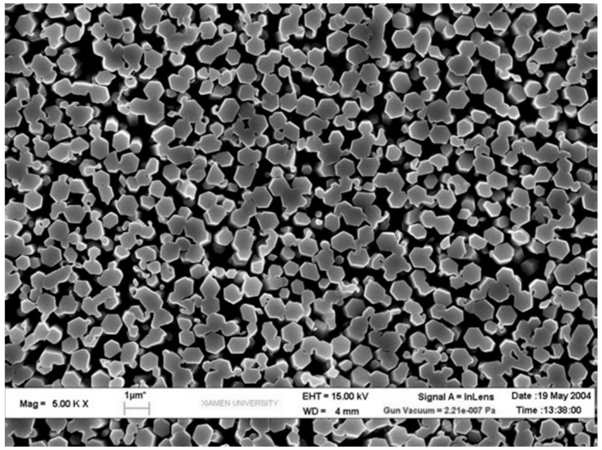


β B_0 （B）

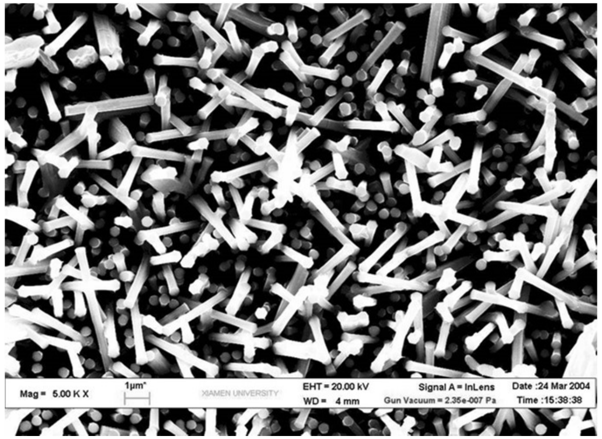
$$h(s)=\int_{-\infty}^{+\infty} g(t)f(s-t)dt \quad \text{or} \quad h(s)=g(s)\otimes f(s)$$

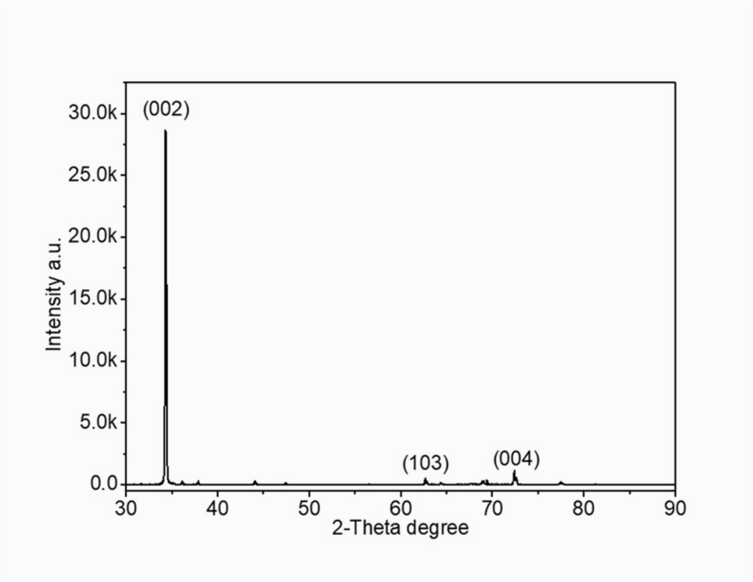
$$F(h(s))=F(g(s))\times F(f(s))$$

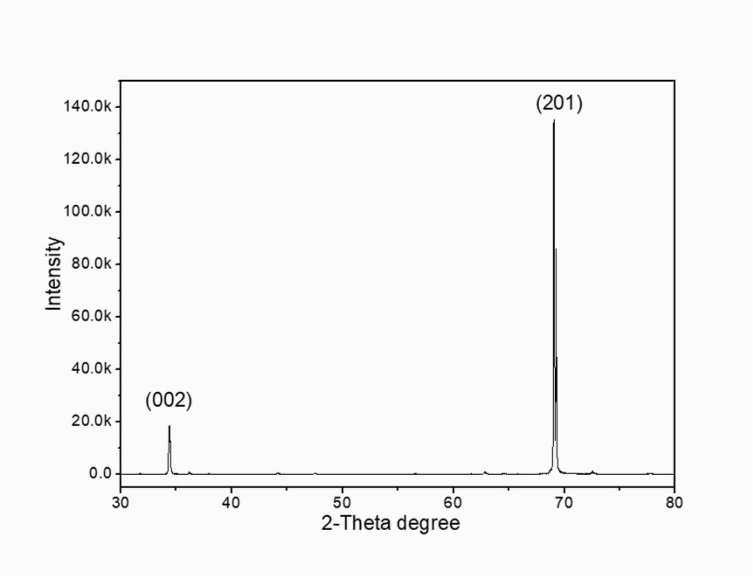
(vi) Texture



ZnO nano-arrays







b. Applications of powder diffractions

Applications

Qualitative Analysis

Quantitative Analysis

Lattice Parameter Determination

Crystallite size / size distribution & Lattice Distortion Analysis (Non-uniform microstrain)

Crystallinity Analysis

Residue Stress Analysis

Texture analysis

Structure Solution and Refinement

Radical distribution function (for amorphous materials)

7.3.5 Electron Diffraction and Neutron Diffraction

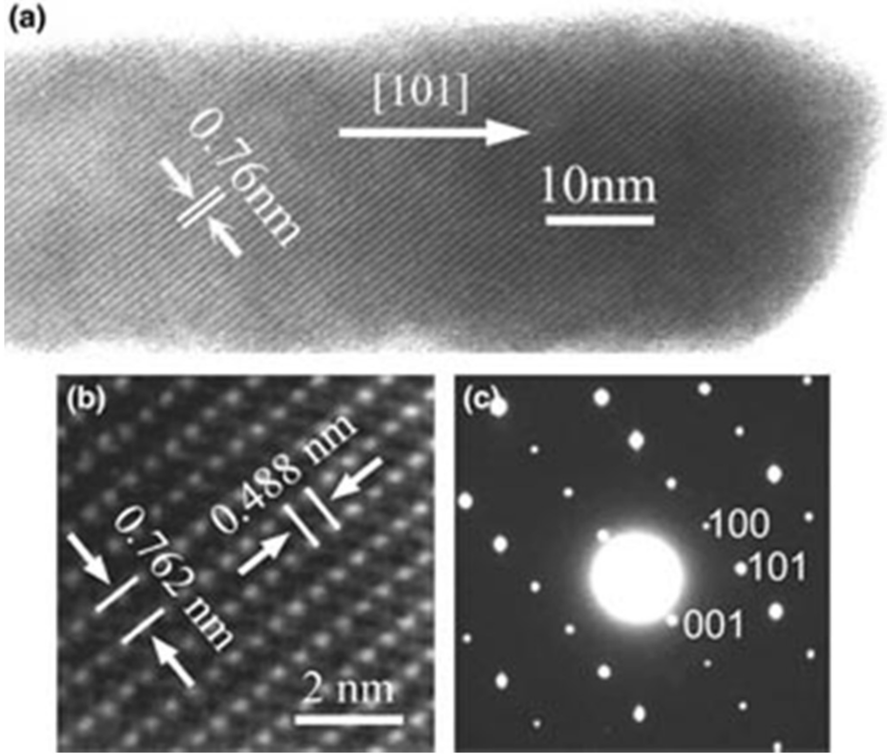
1. Electron Diffraction

de Brogli wave length
of electron in a field V:

$$\lambda = \frac{h}{\sqrt{2m_e eV}}$$

100 kV ---- $\lambda \sim 0.00370$ nm

Atom-level resolution!



a) TEM image of the tip part of one TeO_2 nanorod. (b) Enlarged TEM image. (c) The corresponding electron diffraction pattern.

2. Neutron Diffraction

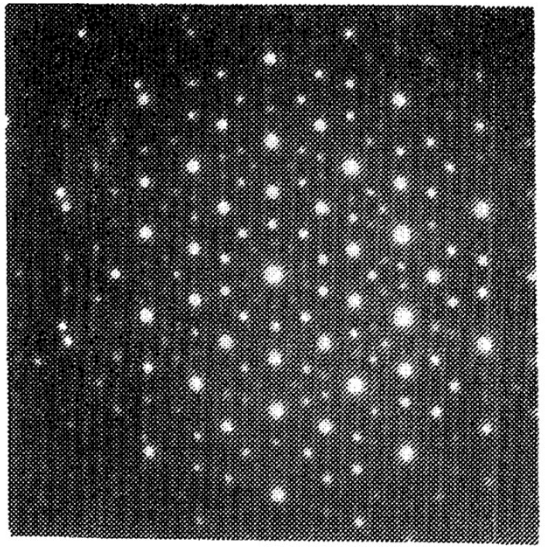
----- Scatterring of atomic nuclear

~ higher atomic resolution

7.4 Quasicrystal, liquid crystal and amorphous

Quasicrystal:

- quasiperiodic crystal
- 5-fold axis occurs in solid state, seemingly challenging the crystallographic theory.



- In 1984, Dan Shechtman et al. reported their finding that the Al-Mn(14 at.%) alloy adopts an icosahedral phase with 5-fold axis. (first observed in 1982.4.8, see Phys. Rev. Lett. 1984, 53, 1951).
- He won the Nobel Prize in Chemistry in 2011.

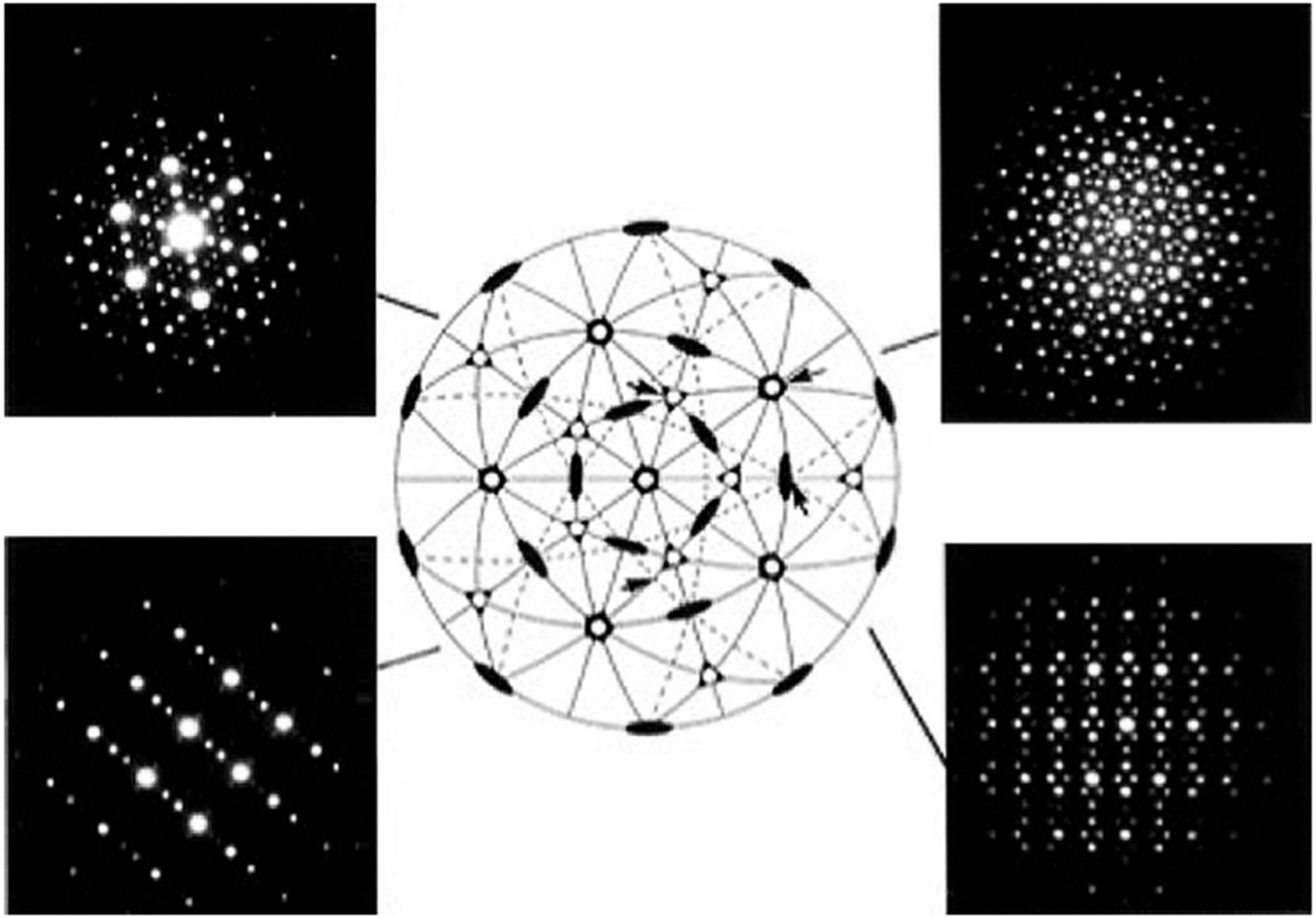
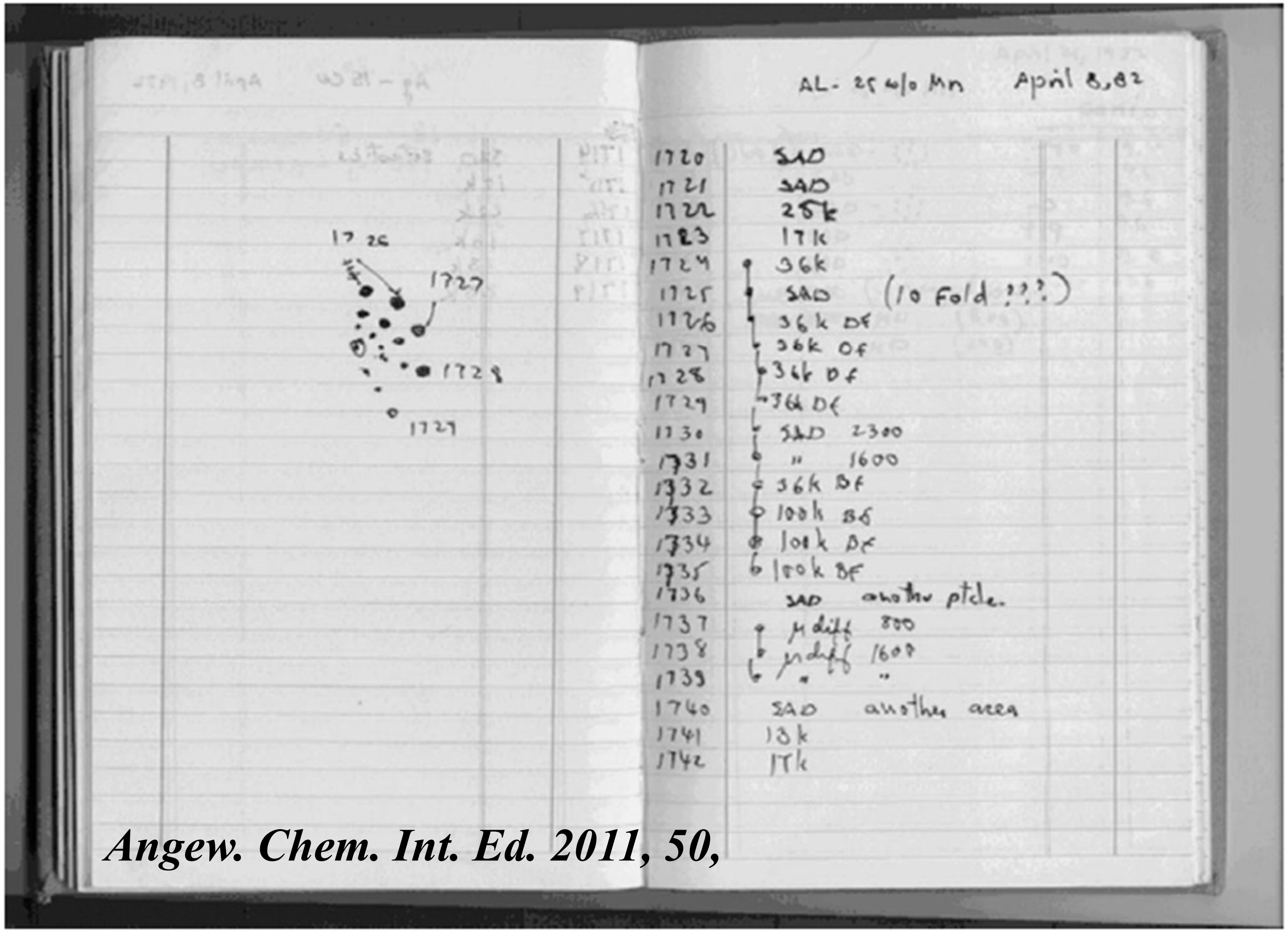


Figure 1. Electron diffraction patterns of the Al-Mn quasicrystal taken along different symmetry directions indicating icosahedral diffraction symmetry. Reprinted from Ref. [1].



AL- 25 w/o Mn   April 8,82

1720	SAD	
1721	SAD	
1722	25k	
1723	17k	
1724	36k	
1725	SAD	(10 Fold ???)
1726	36k DF	
1727	36k DF	
1728	36k DF	
1729	36k DF	
1730	SAD	2300
1731	"	1600
1732	36k BF	
1733	100k BF	
1734	100k DF	
1735	100k BF	
1736	SAD	another ptcle.
1737	μ diff	800
1738	μ diff	1600
1739	"	"
1740	SAD	another area
1741	13k	
1742	17k	

Angew. Chem. Int. Ed. 2011, 50,

Figure 2. Shechtman's notes of April 8, 1982, with the observation of tenfold symmetry highlighted by three question marks.

Even his cooperator, J. W Cahn, thought that the pheonomenon was resulted from twinning of single crystals!

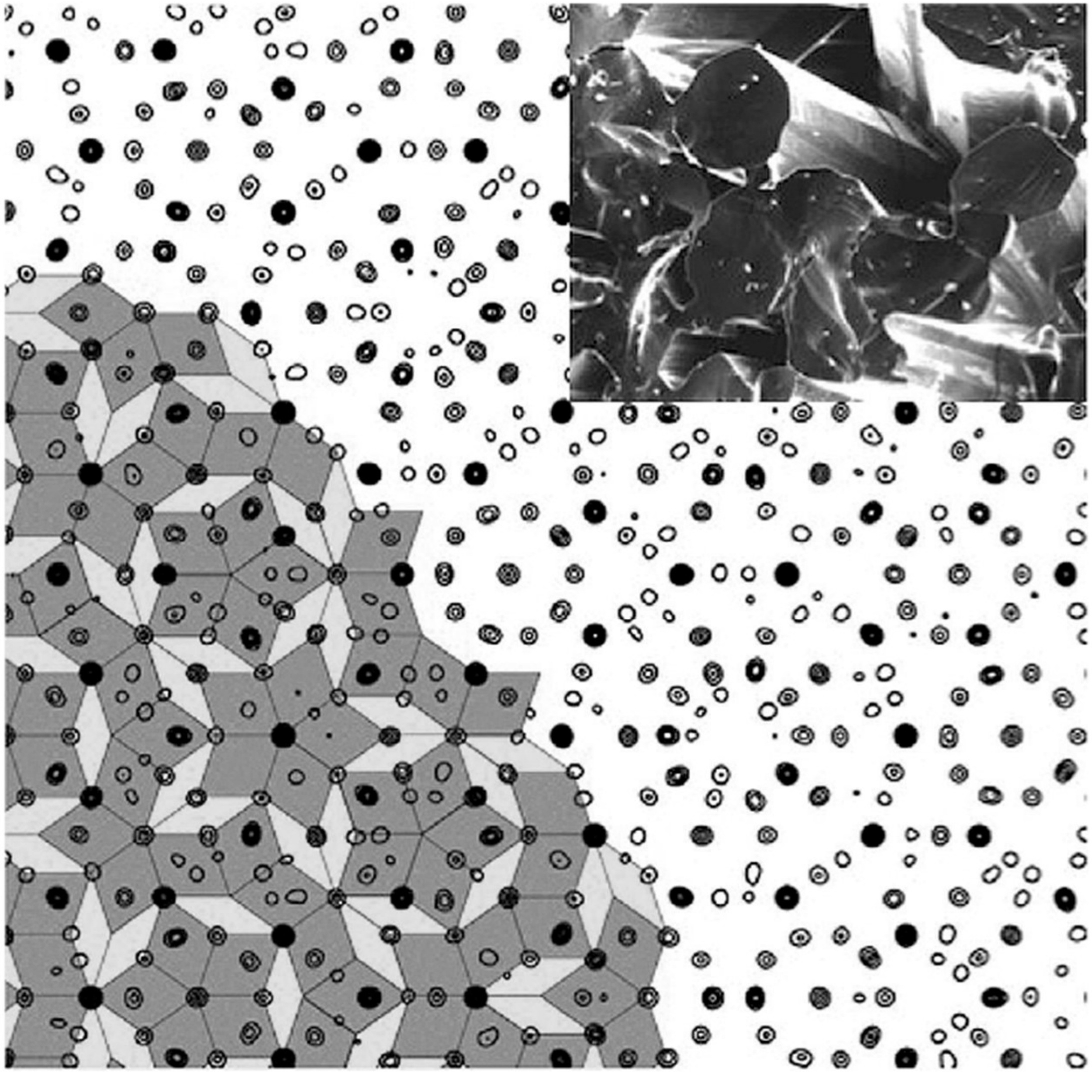


Figure 6. Projected electron density map of decagonal Al-Co-Ni with underlying Penrose tiling. In the insert (upper right), some intergrown decaprismatic quasicrystals are depicted.

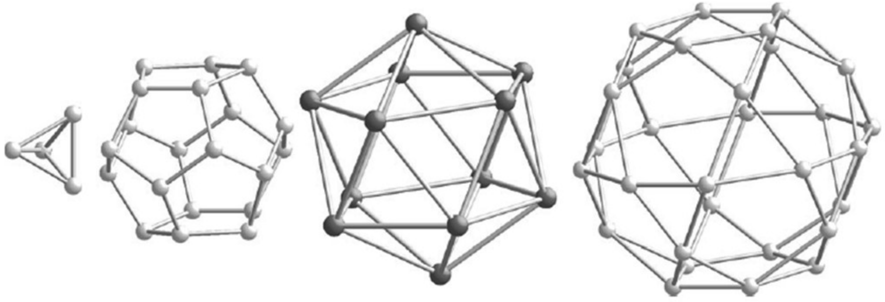
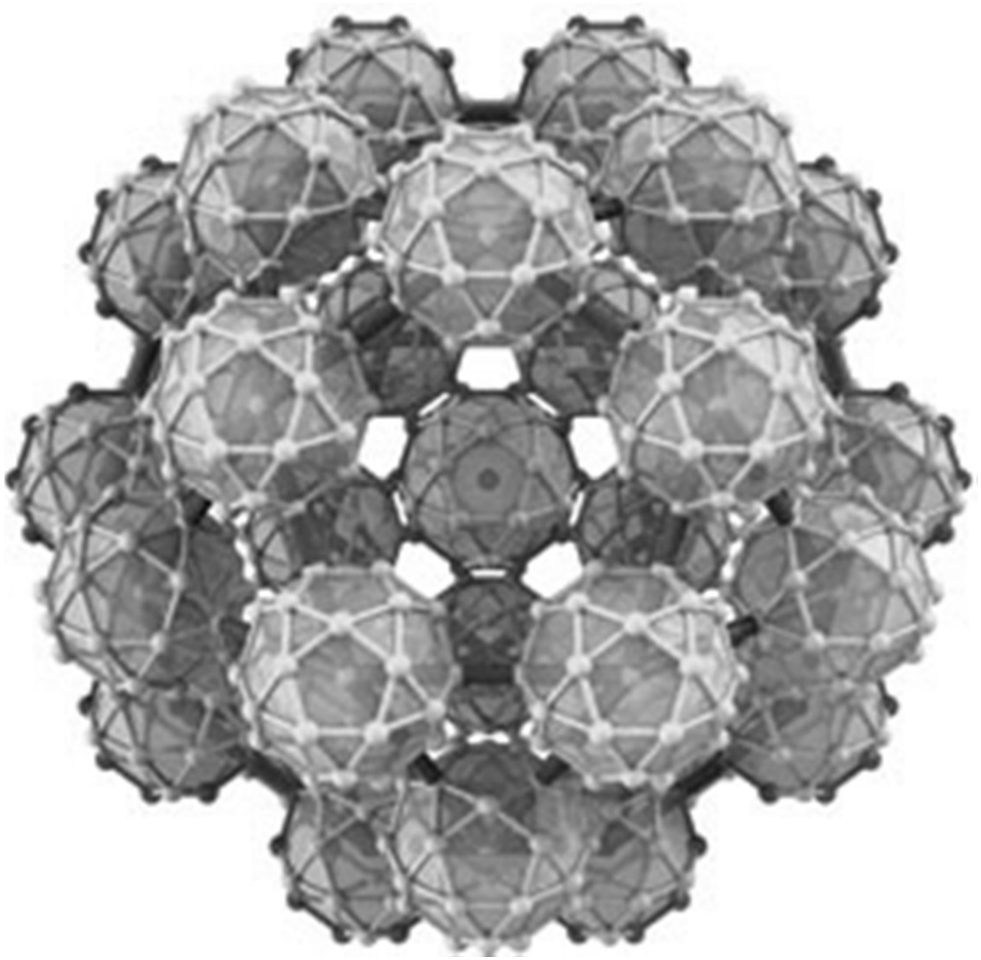


Figure 5. Shell structure of the $Cd_{54}Yb_{12}$ Tsai cluster (Cd light spheres, Yb dark spheres).



An icosahedral Yb-Cd quasicrystal is composed of an aperiodic ordered arrangement of YbCd clusters (yellow and blue spheres at the vertices of the polyhedra

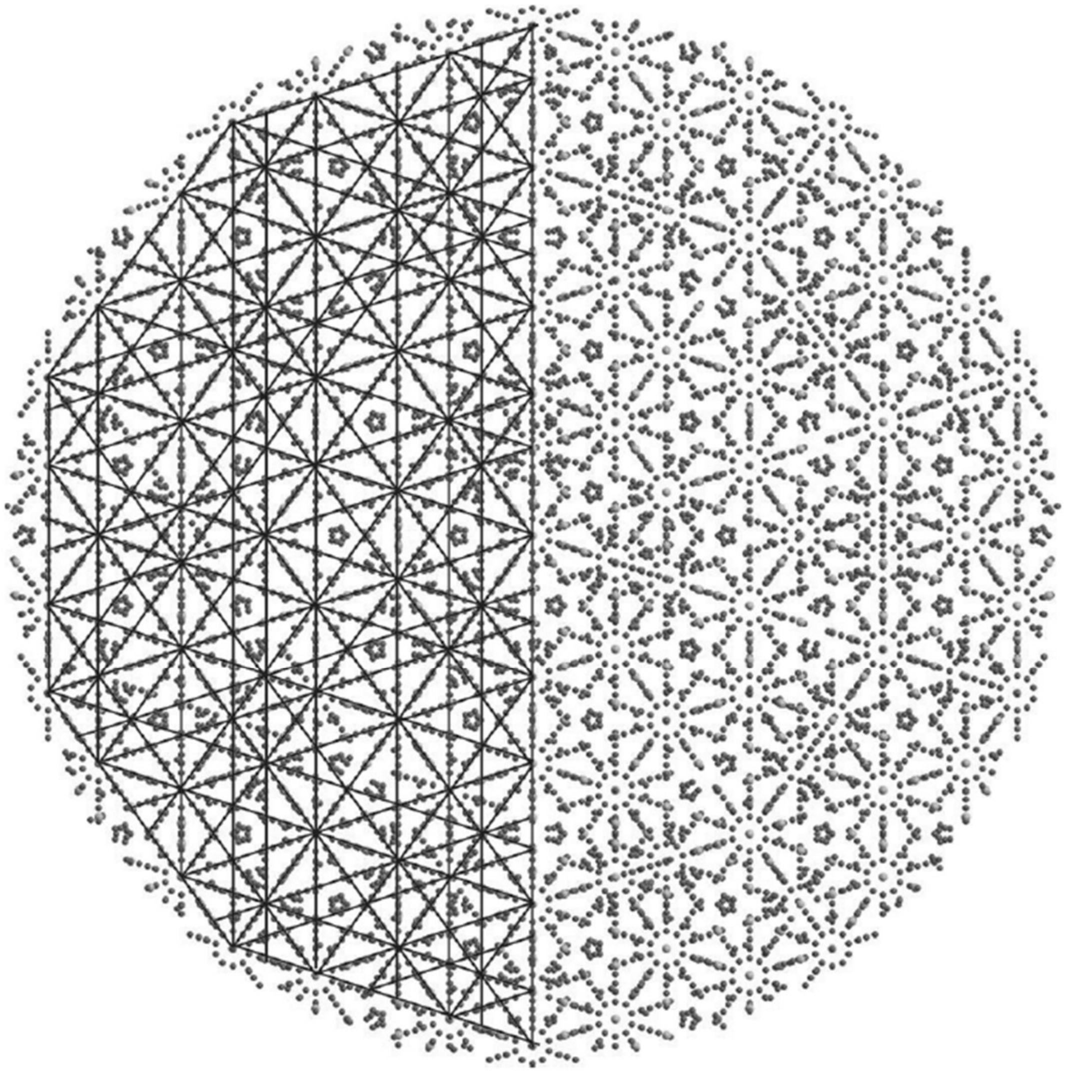
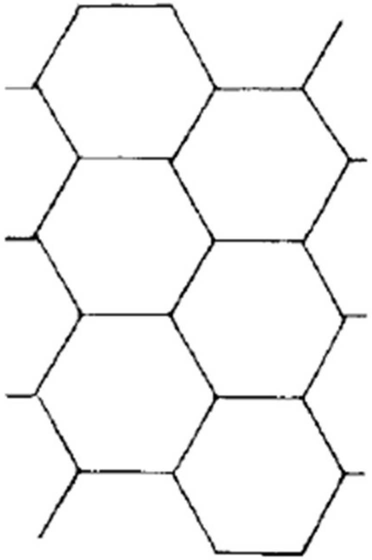


Figure 7. Projection of a spherical section (diameter 100 Å) of the structure of icosahedral Cd-Yb[20] along a fivefold axis. Almost all atoms are arranged in flat atomic layers, forming a framework compatible with fivefold symmetry. The atomic layers interpenetrate each other in a way that is only possible in quasiperiodic structures.

Crystal



**Translation symmetry,
Long-range order,
Directional.**

Quasi-crystal

No translation symmetry;

Long-range order, directional.

3D quasicrystal:

Icosahedral phase in Al-Mn, Ti_2Ni, Al-Li-Cu, Mg-Al-Zn alloys.

2D quasicrystal:

With 1D translation symmetry and 2D quasiperiodicity.

8-fold, 10-fold quasicrystals in some alloys.

History of quasicrystal concept

(extracted from wikipedia)

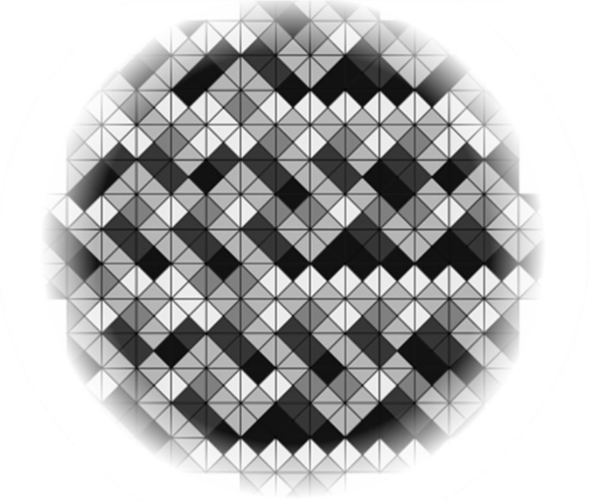
1. Quasicrystal-like structures had been known well before the 20th-century, e.g., tiles in a medieval islamic mosque in Iran.

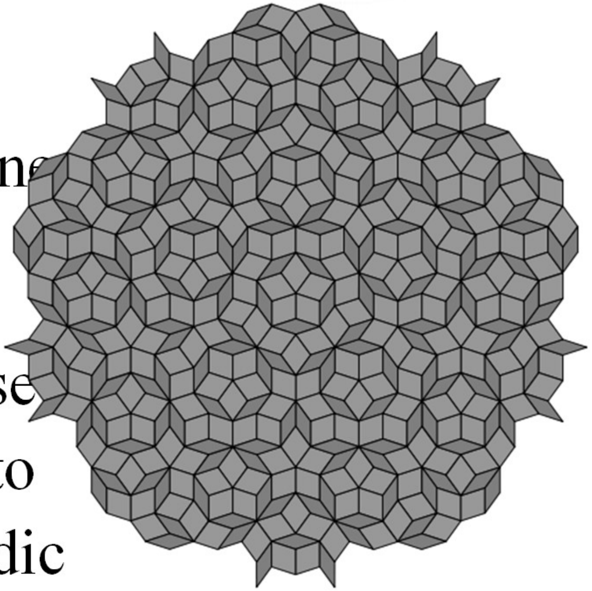
2. In 1961, Hao Wang proposed a mathematic problem related to the planar tiling.

3. In 1966, Wang's student, Robert Berger, constructed a set of some 20,000 square tiles (now called Wang tiles), which can tile the plane aperiodically.

4. In particular, in 1976, Roger Penrose propose a set of just two tiles, up to rotation, (referred to as Penrose tiles) that produced only non-periodic tilings of the plane.

Wang Tiles





Penrose Tiling

5. In 1982, Alan Mackay showed experimentally that the diffraction pattern from the Penrose tiling had a two-dimensional Fourier transform consisting of sharp 'delta' peaks arranged in a fivefold symmetric pattern. (Physica A, 1982, 114, 609)

6. The history of quasicrystals begins with the 1984 paper "Metallic Phase with Long-Range Orientational Order and No Translational Symmetry" where Dan Shechtman *et al.* demonstrated a clear diffraction pattern with a fivefold symmetry.

7. The term *quasicrystal* was first used in print shortly after the announcement of Shechtman's discovery, in a paper by Steinhardt and Levine. (Phys. Rev. Lett. 1984, 53,2477)

8. At the end of the 1980s, the idea of quasicrystal became widely acceptable!

Liquid crystals

- Crystalline solid: anisotropic
- Liquid: isotropic
- Liquid crystal: anisotropic!

  Liquids with well-ordered, crystal-like structures.

More details of liquid crystals can be learnt in material science!

Chapter 7

Key points/concepts

1. Lattice of crystal structure: translation symmetry

   a lattice point = a structure motif   -- unit cell

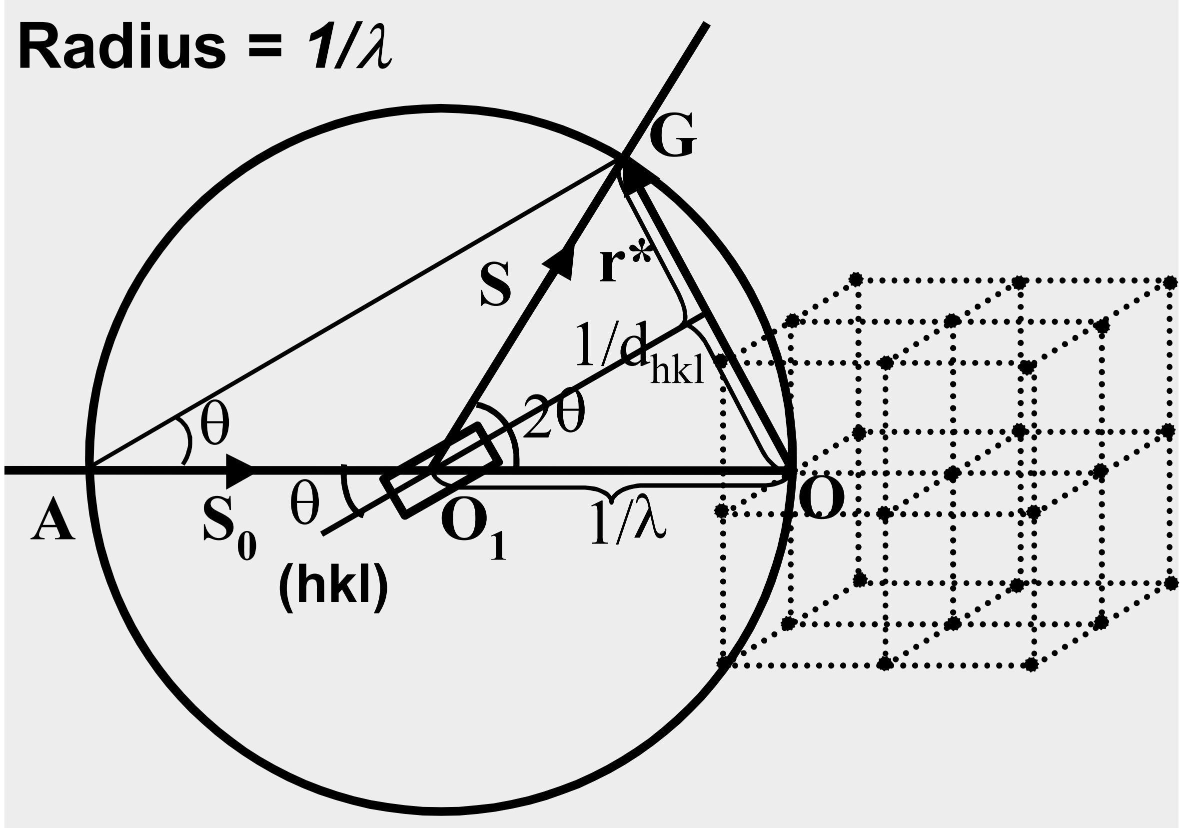
2. Crystal systems (7), Bravais Lattice (14)
3. Symmetry operations (point & translation), Crystallographic point groups(32), space groups (230), equivalent positions.
4. Miller index of crystal plane，d-spacing etc.
5. X-ray diffraction, Laue equation, Bragg's Law, reciprocal lattice, Ewald sphere, structural factor, system absence, general process of x-ray crystal structure determination.

X-ray diffraction, Bragg’s Law, Ewald sphere

$$2d_{hkl}\sin\theta = \lambda$$ **Bragg’s law**

Ewald sphere + reciprocal lattice

$$|OG| = 2|O_1O^*|\sin\theta = (2/\lambda)\sin\theta = 1/d_{hkl}$$



Directions of detected X-ray diffraction beams: {2θ}

$\sin^2\theta_1:\sin^2\theta_2:\ldots.:\sin^2\theta_n$

indexing

Crystal system, Bravais lattice, cell parameters etc.

F_{hkl} & $\rho(x,y,z)$

- # Structure factor & systematic absence

$$I_{hkl} = K\left|F_{hkl}\right|^2$$

Structure factor:

$$F_{hkl} = \sum_{j=1}^{n} f_j e^{2\pi i (hx_j + ky_j + lz_j)}$$

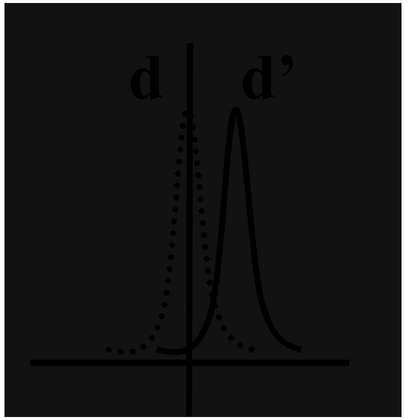
Phase difference between the scattered and incident x-ray over atom j.

Sum over all atoms within a unit cell.

f_j: atomic scattering factor defined by atomic electron density distribution.

- **some reflections/diffractions will be systematically absent ($F_{hkl} = 0 \rightarrow I_{hkl} = 0$) in case a crystall lattice has centering, glide plane and screw axis.**

Further applications of X-ray diffraction



Δ**d**$_{hkl}$ **vs.** $\Delta\theta_{hkl}$

a) Change of specific d-spacing

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

b) Size effect of microcrystal—broadening of diffraction peaks

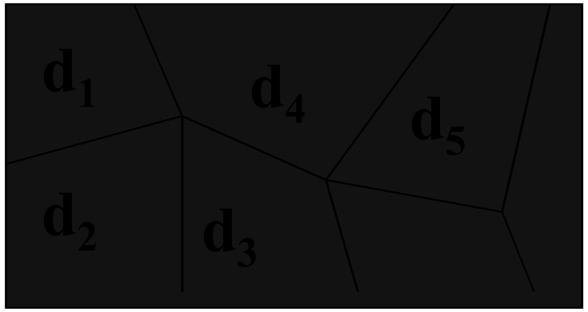
$$I \propto \left|F_{hkl}\right|^2 N_1^2 N_2^2 N_3^2 = \left|F_{hkl}\right|^2 \left|A\right|^2$$

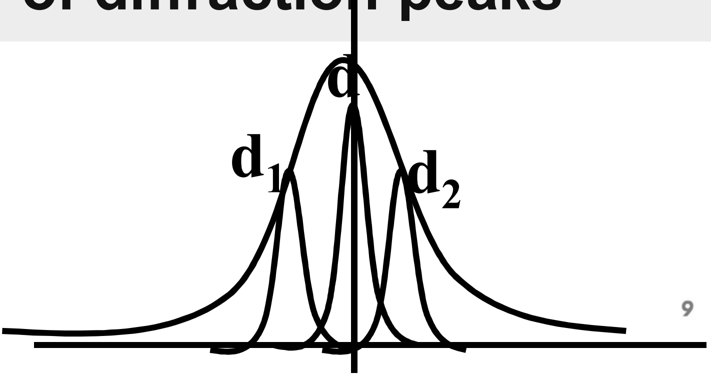
Scherrer formula

(size: 1-100nm)

$$D_{hkl}=\frac{K\cdot\lambda}{\beta\cdot\cos\theta_{hkl}}=\frac{K\cdot\lambda}{(B-B_0)\cdot\cos\theta_{hkl}}$$

c) Deformation of lattice—broadening of diffraction peaks





In the diffraction direction, the difference between the incident and the diffracted beam through any two lattice points must be an integral number of wavelengths.

The lattice vector from (000) to (mnp): $\boldsymbol{T}_{\mathrm{mnp}} = \mathrm{m}\boldsymbol{a} + \mathrm{n}\boldsymbol{b} + \mathrm{p}\boldsymbol{c}$

The differences in wavelengths for observed diffractions:

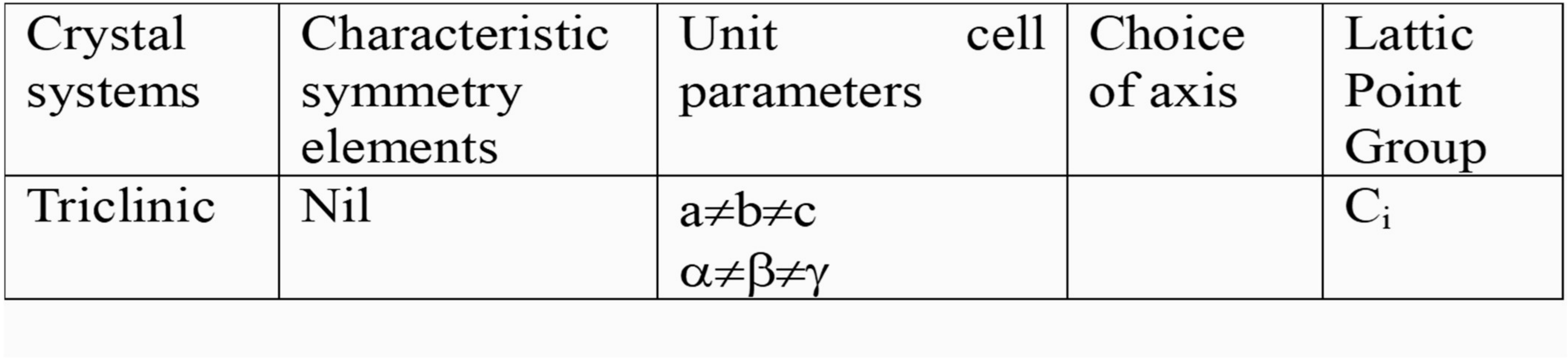
$\Delta = \boldsymbol{T}_{\mathrm{mnp}} \cdot (\boldsymbol{S}-\boldsymbol{S}_0)$

$= (\mathrm{m}\boldsymbol{a} + \mathrm{n}\boldsymbol{b} + \mathrm{p}\boldsymbol{c}) \cdot (\boldsymbol{S}-\boldsymbol{S}_0)$

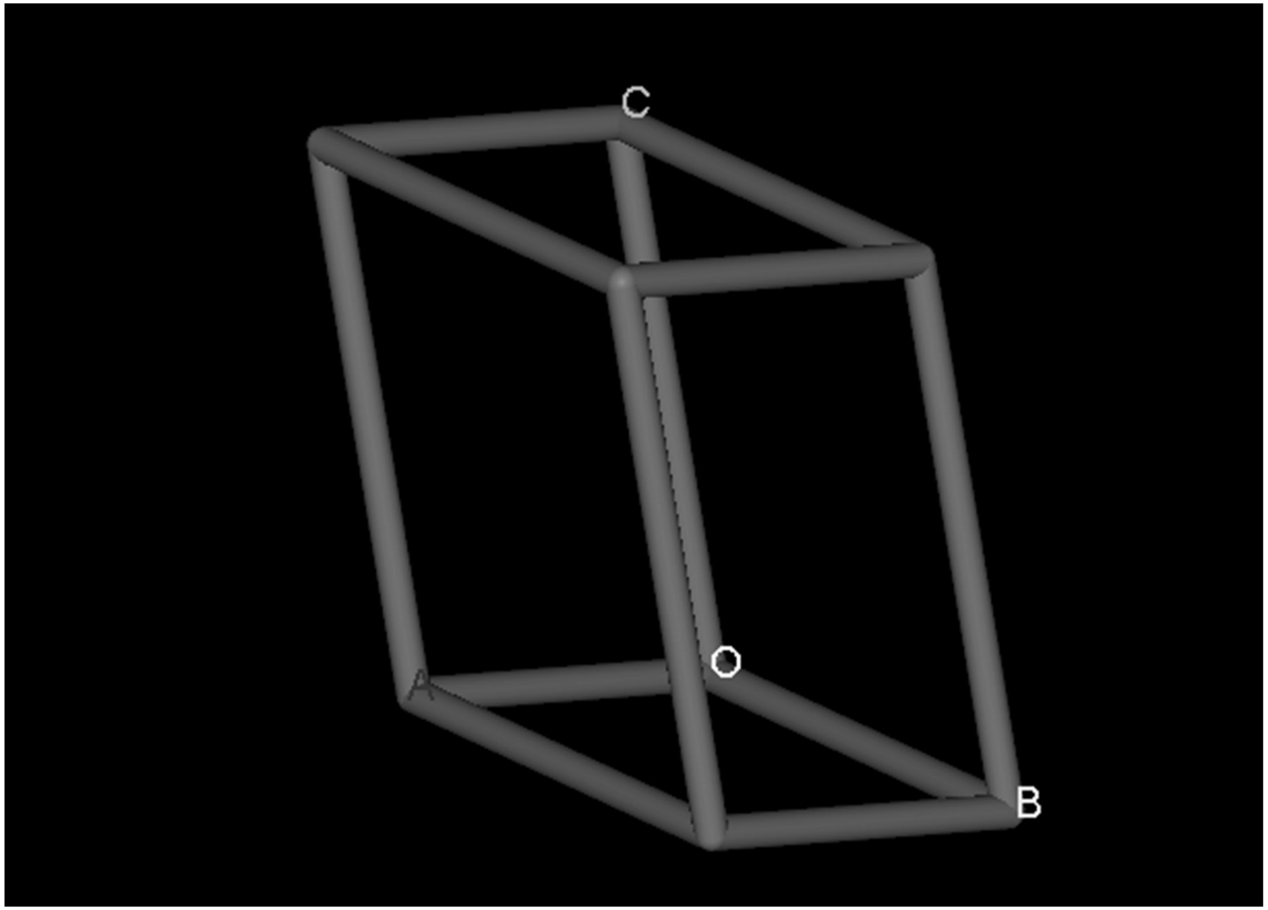
$= \mathrm{m}\boldsymbol{a} \cdot (\boldsymbol{S}-\boldsymbol{S}_0) + \mathrm{n}\boldsymbol{b} \cdot (\boldsymbol{S}-\boldsymbol{S}_0) + \mathrm{p}\boldsymbol{c} \cdot (\boldsymbol{S}-\boldsymbol{S}_0)$

$= mh\lambda + nk\lambda + pl\lambda$

$= (mh+nk+pl)\lambda$



Crystal systems	Characteristic symmetry elements	Unit cell parameters	Choice of axis	Lattic Point Group
Triclinic	Nil	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$		C_i



2D lattices:

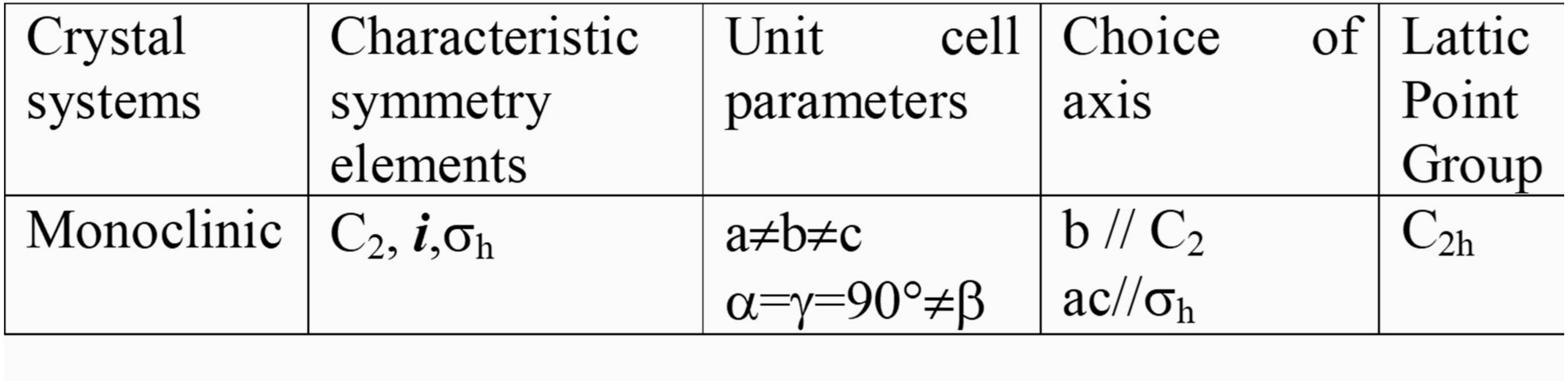
3 parellelograms

Inversion center:

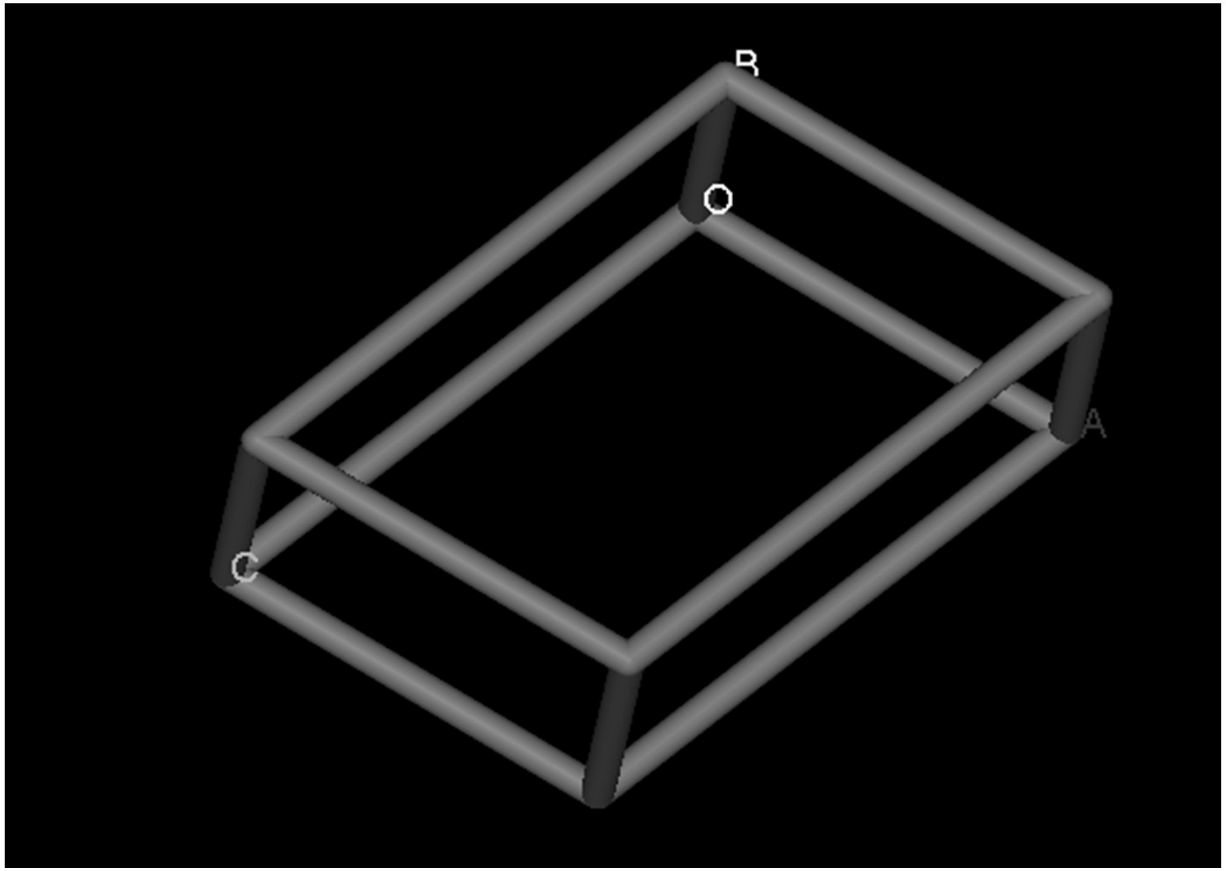
(0,0,0); (1/2,1/2,1/2)

(0,0,1/2), (1/2,0,0), (0,1/2,0);

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



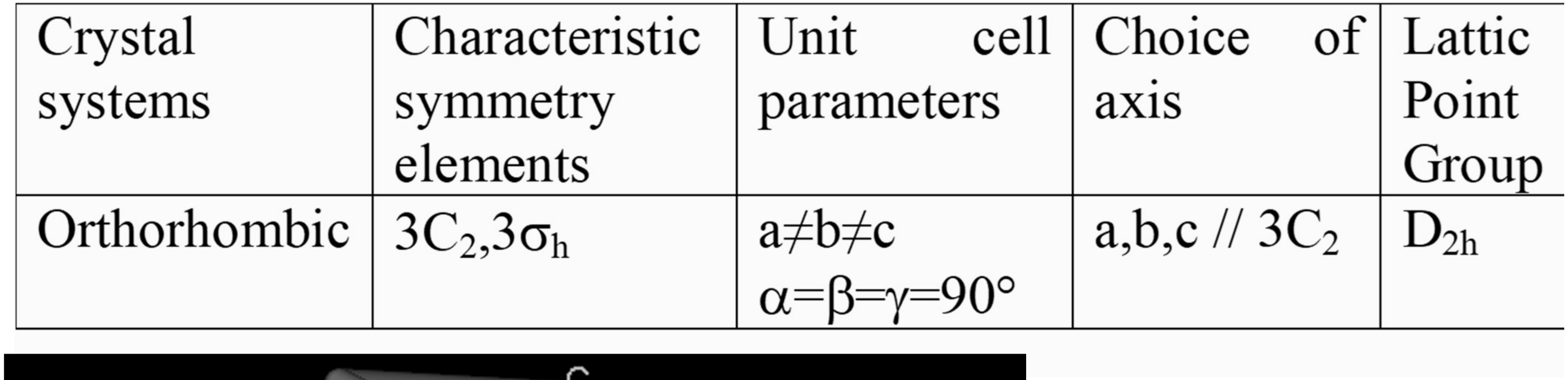
Crystal systems	Characteristic symmetry elements	Unit cell parameters	Choice of axis	Lattic Point Group
Monoclinic	C_2, $\boldsymbol{i}$,σ_h	$a \neq b \neq c$ $\alpha = \gamma = 90° \neq \beta$	b // C_2 ac//σ_h	C_{2h}



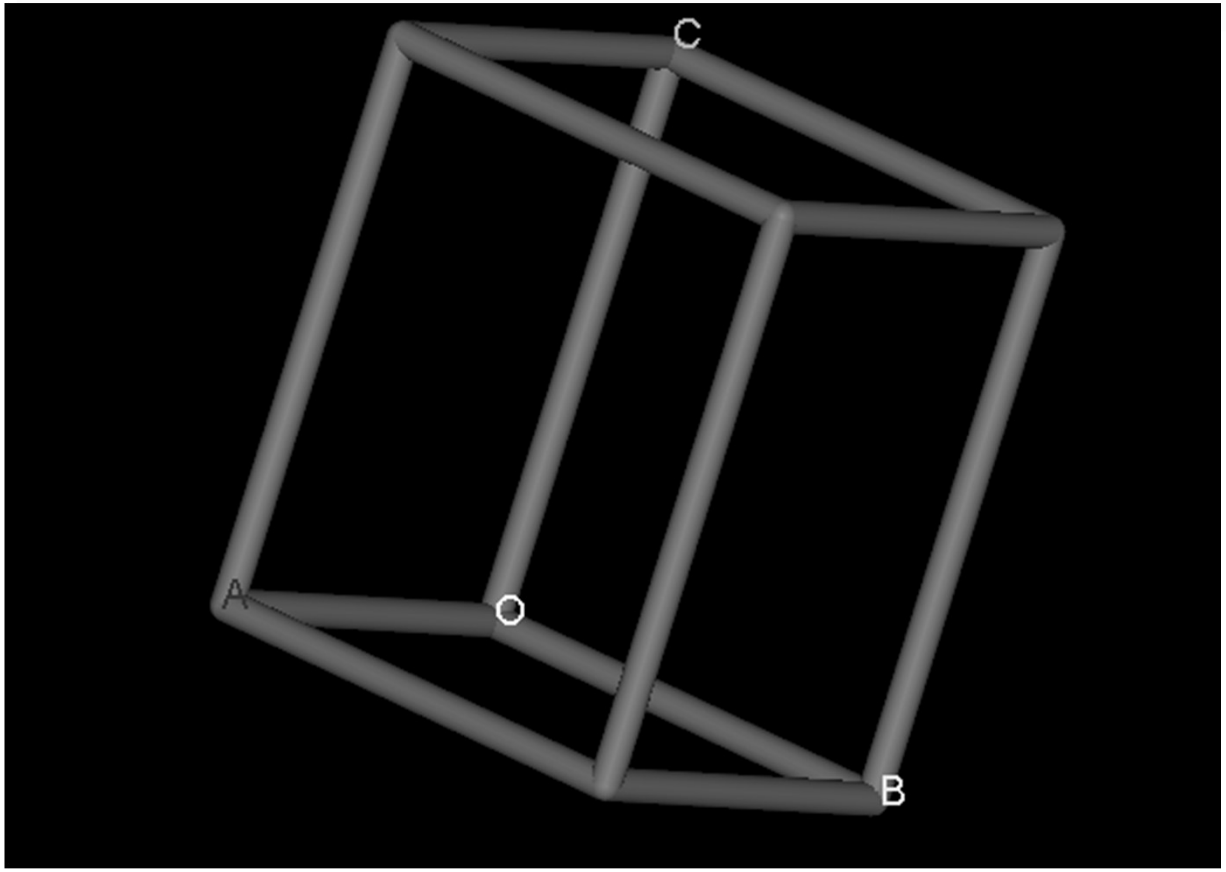
2D lattices:

1 parellelogram

2 rectangles.

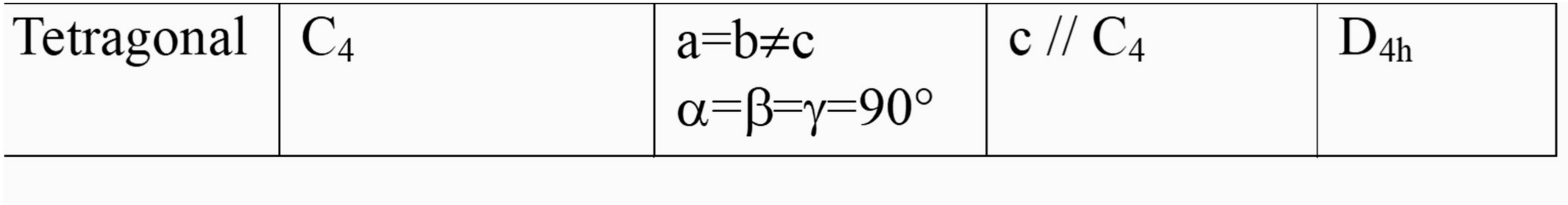


Crystal systems	Characteristic symmetry elements	Unit cell parameters	Choice of axis	Lattic Point Group
Orthorhombic	$3C_2, 3\sigma_h$	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$	a,b,c // $3C_2$	D_{2h}

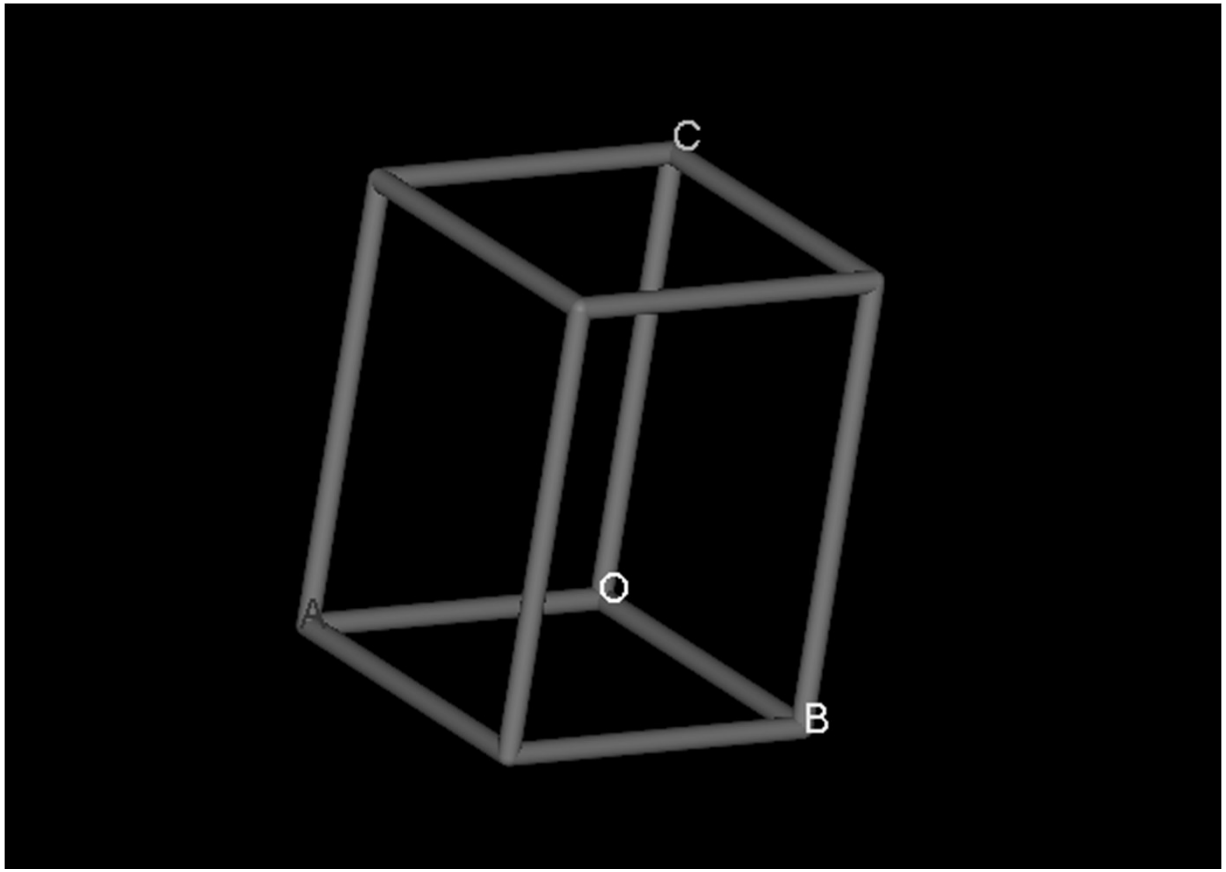


2D lattices:

3 rectangles.



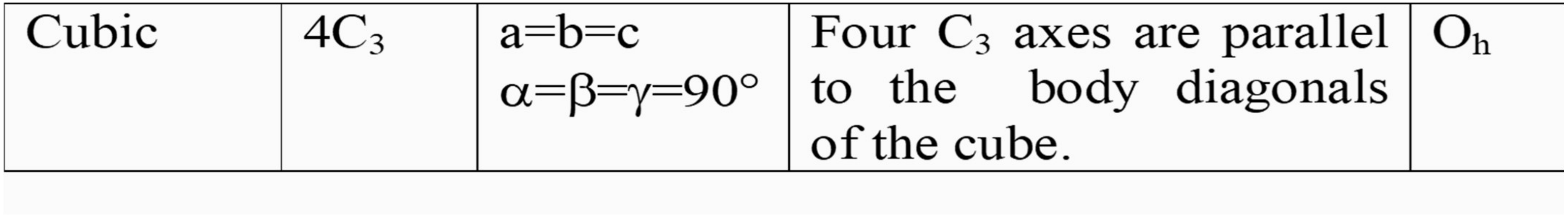
Tetragonal	C_4	$a=b\neq c$ $\alpha=\beta=\gamma=90°$	$c \mathbin{//} C_4$	D_{4h}



2D lattices:

1 square

2 rectangles.

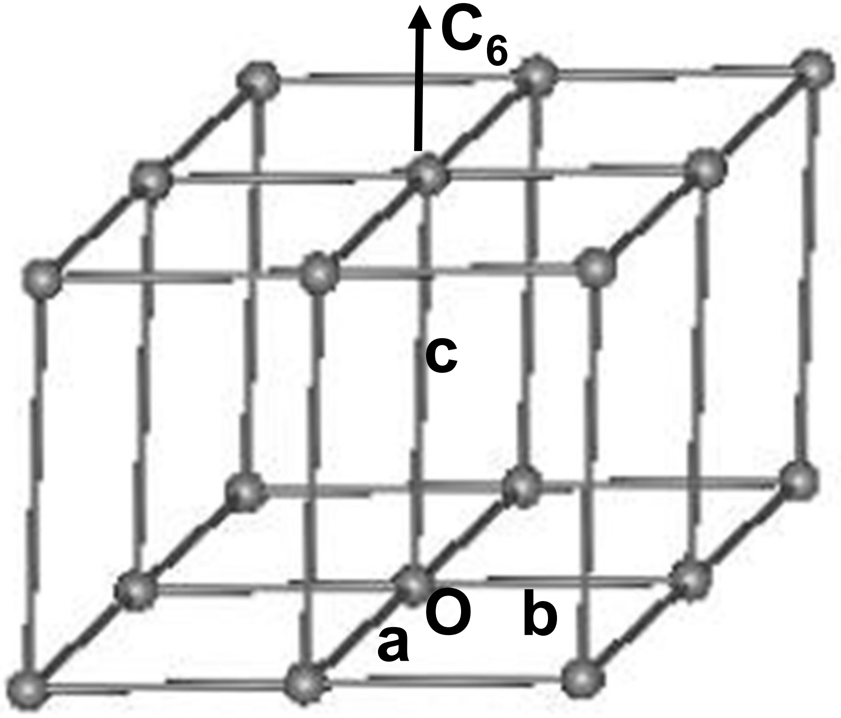


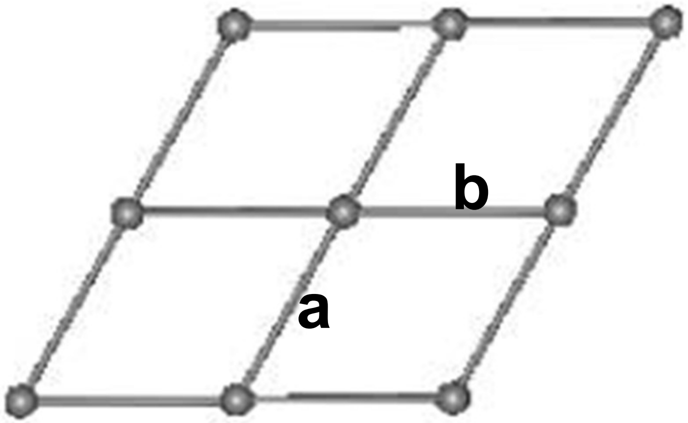
Cubic	$4C_3$	$a=b=c$ $\alpha=\beta=\gamma=90°$	Four C_3 axes are parallel to the body diagonals of the cube.	O_h

2D lattices:

3 squares

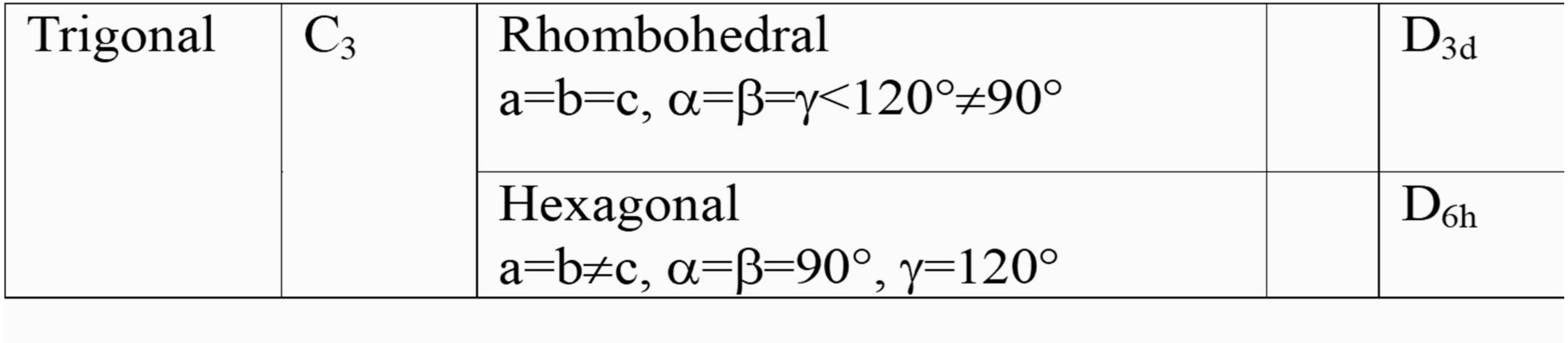
Hexagonal	C_6, σ_h	$a=b\neq c$ $\alpha=\beta=90°$ $\gamma=120°$	c // C_6	D_{6h}



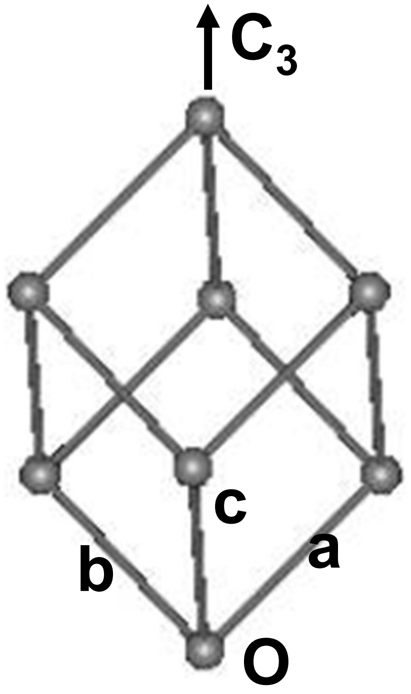


2D lattices:

1 hexagon + 2 rectangles.



Trigonal	C_3	Rhombohedral $a=b=c$, $\alpha=\beta=\gamma<120°\neq 90°$		D_{3d}
		Hexagonal $a=b\neq c$, $\alpha=\beta=90°$, $\gamma=120°$		D_{6h}



Rhombohedral