Chapter 7

Introduction to Crystallography

Diamonds

7.1 **periodicity and lattices of crystal structure**

7.1.1 The characteristics of crystal structure

1. A few definitions:

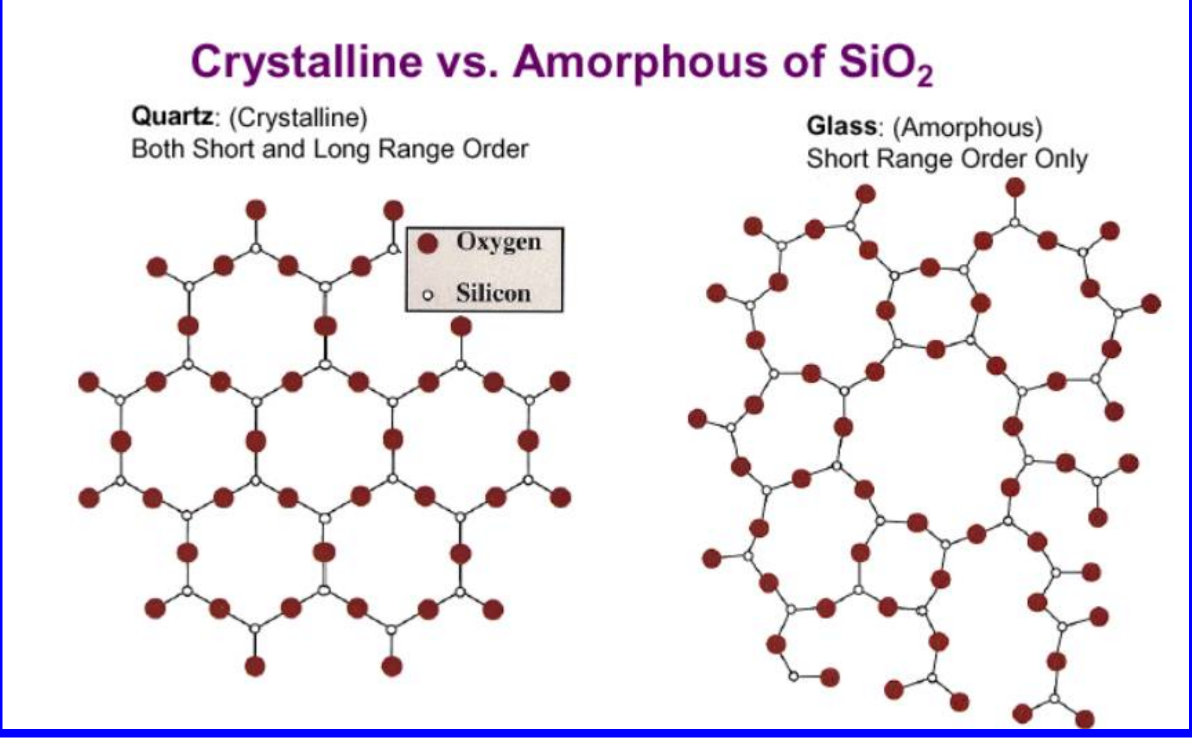
- **Solids can be divided into to primary categories, crystalline and amorphous.**

- **Crystalline Solids that are built from atoms or molecules arranged in a periodic manner in space.**
- **Amorphous Solids posses short range order only. They are not related through symmetry.**

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

Crystals:

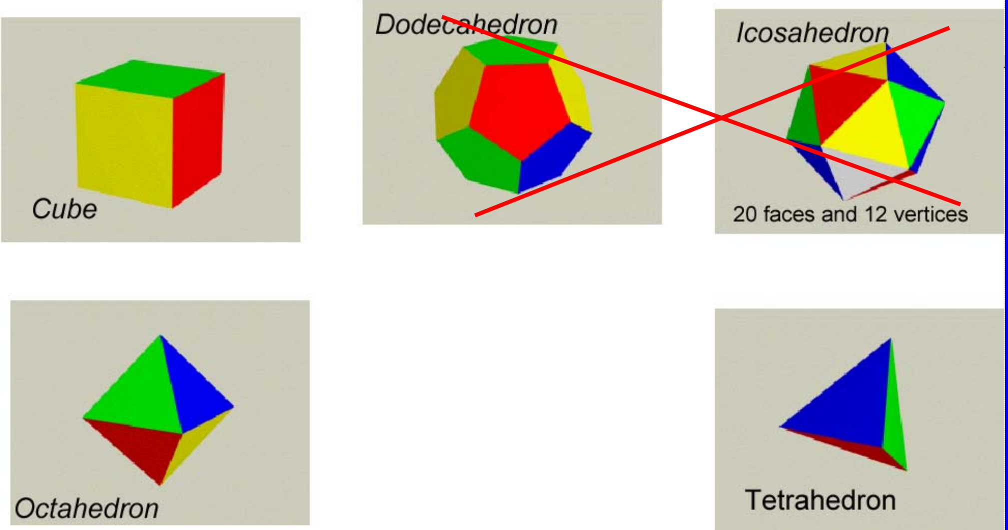
Crystals are solids that are built from atoms or molecules arranged in a periodic manner in space.

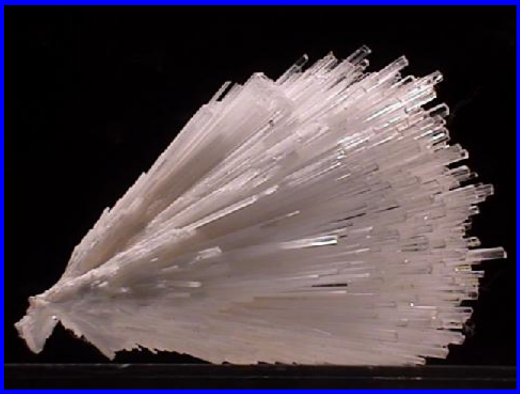


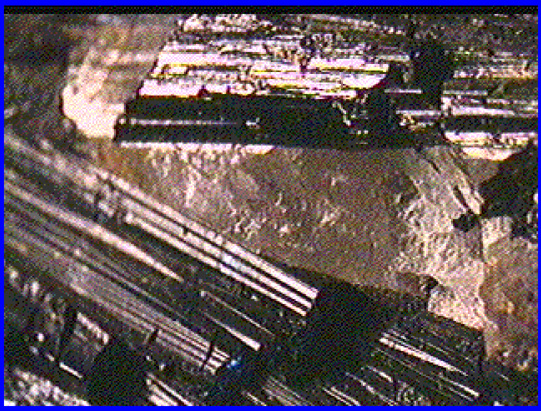
2. Fundamental characteristics of crystal

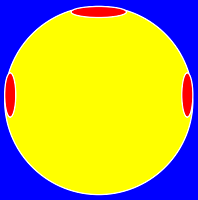
- Spontaneous formation of polyhedral shapes

$$F+V=E+2$$

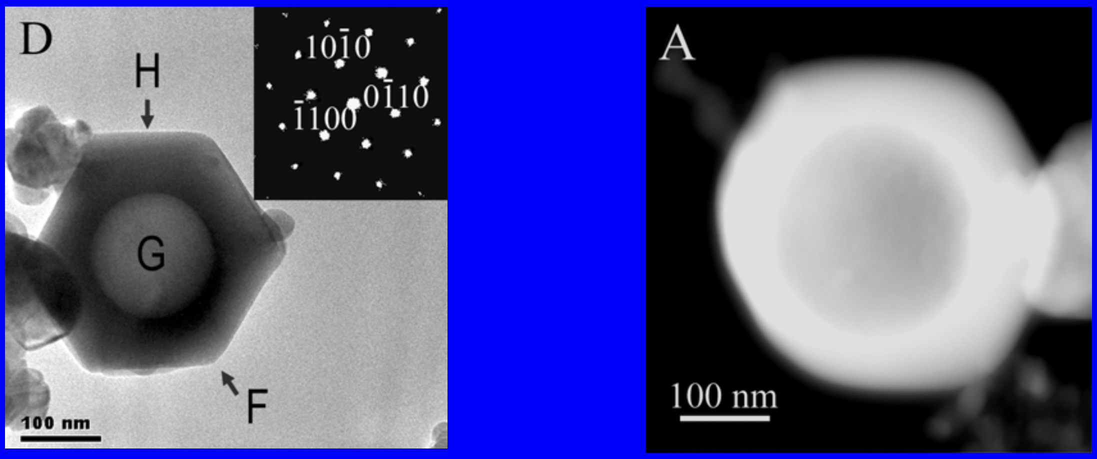






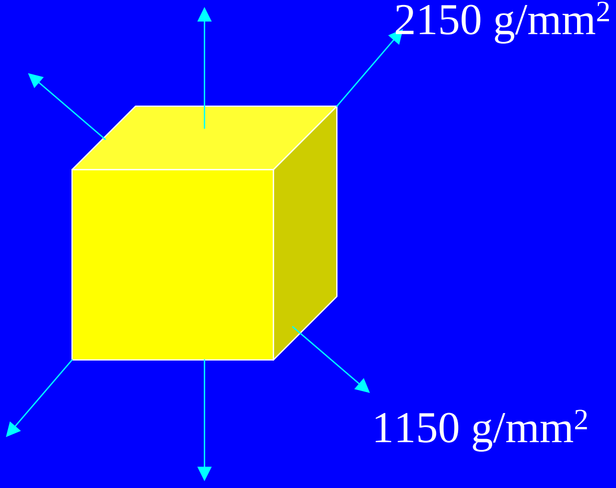


Single crystal gold bead with naturally formed facets



HRTEM images of hollow beads

- Anisotropy

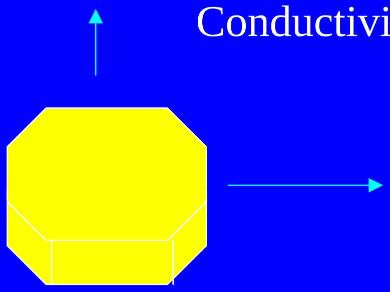


2150 g/mm^2

1150 g/mm^2

570 g/mm^2

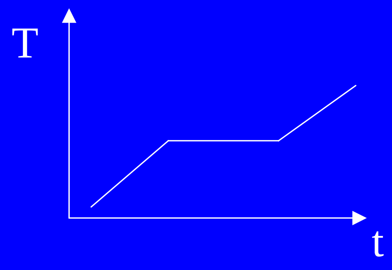
NaCl



Conductivity

Graphite

- Definite sharp melting points



- Symmetry

- X-ray diffraction by crystals

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. The lattice and its unit in 1D:

$$T = m\underline{a} \quad (m = 0, \pm 1, \pm 2, \ldots)$$

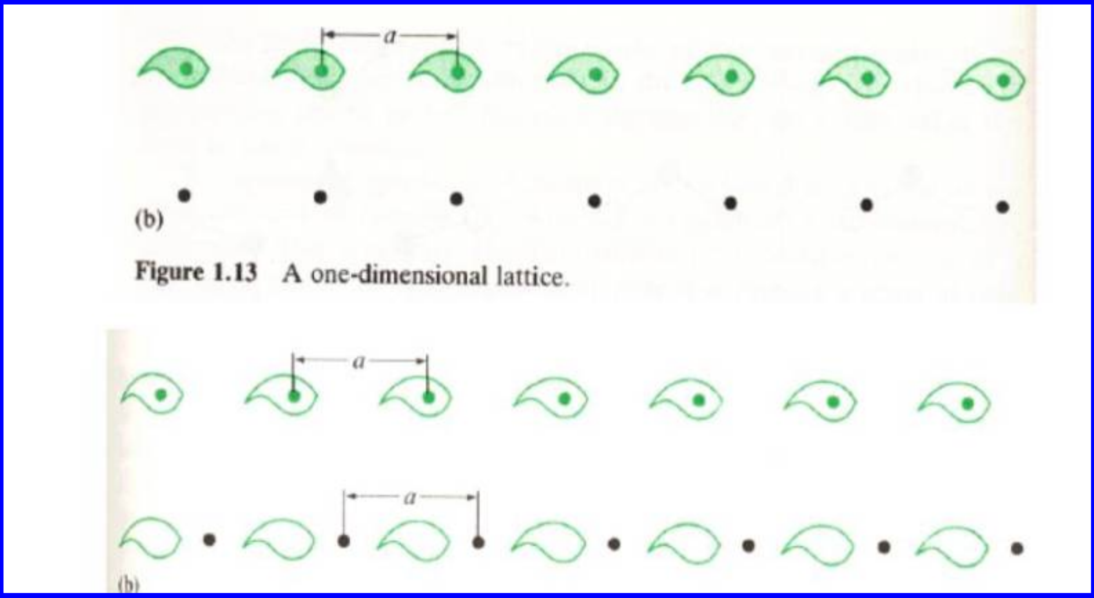
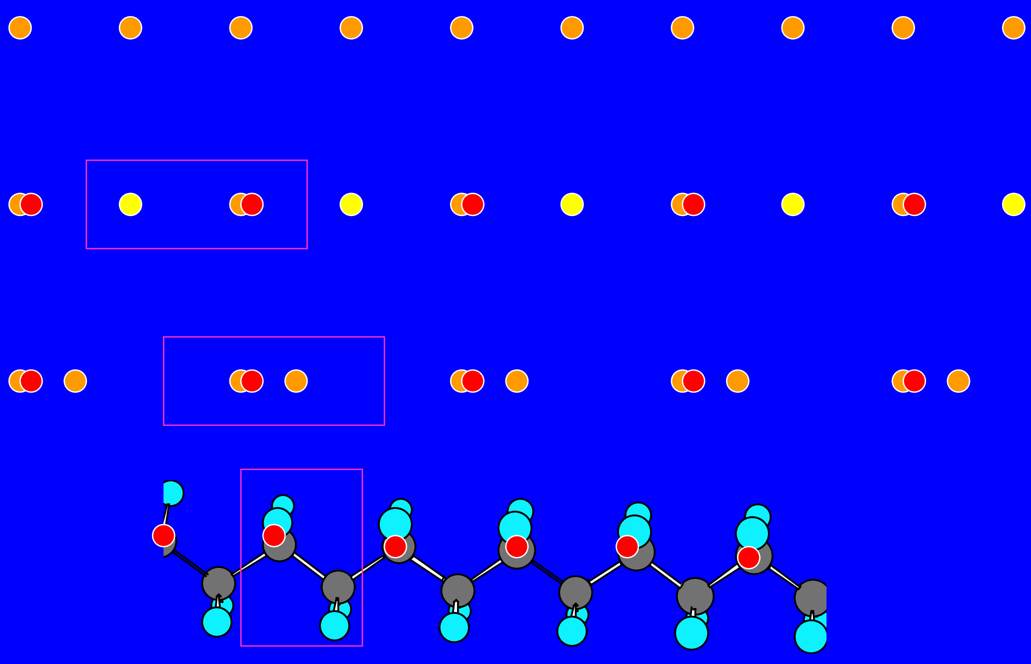


Figure 1.13 A one-dimensional lattice.

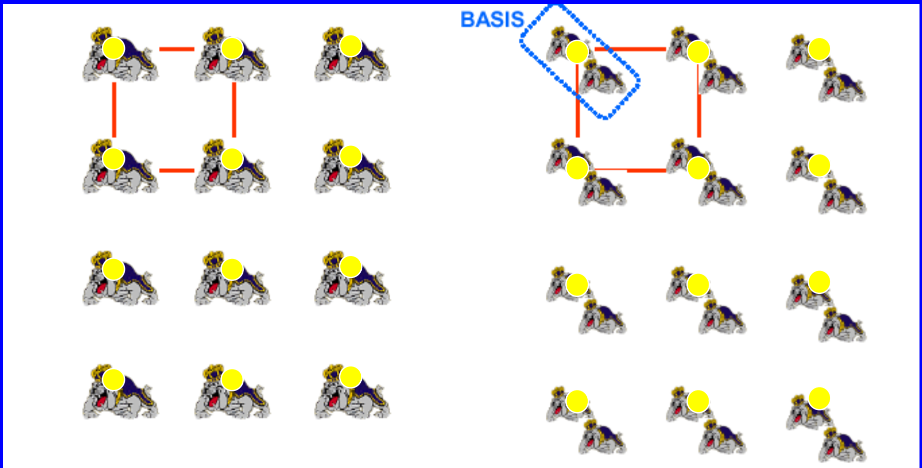
unit cell and its choice for one-dimensional lattice



One dimensional lattice

b. Lattice and its unit in 2D:

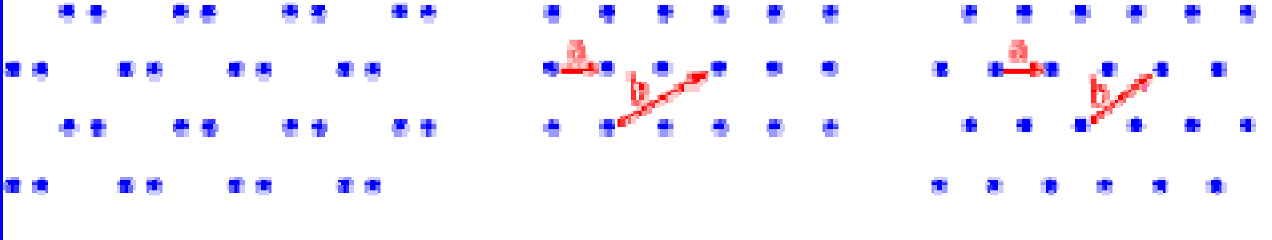
$T = m\underline{a} + n\underline{b}$（m, n = 0,±1, ± 2，…)



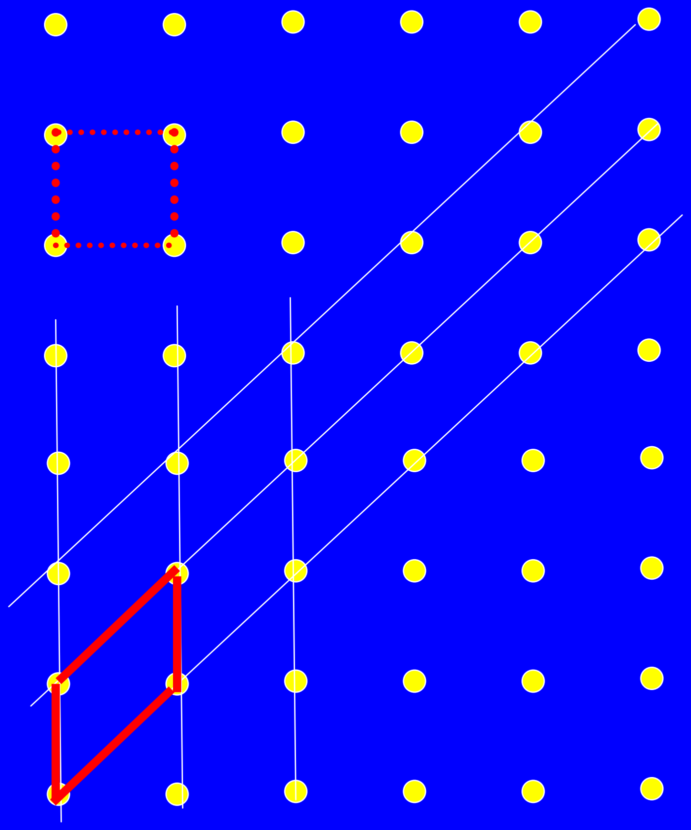
- Crystal structure = lattice + structural motif (basis)

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.



Primitive Cell

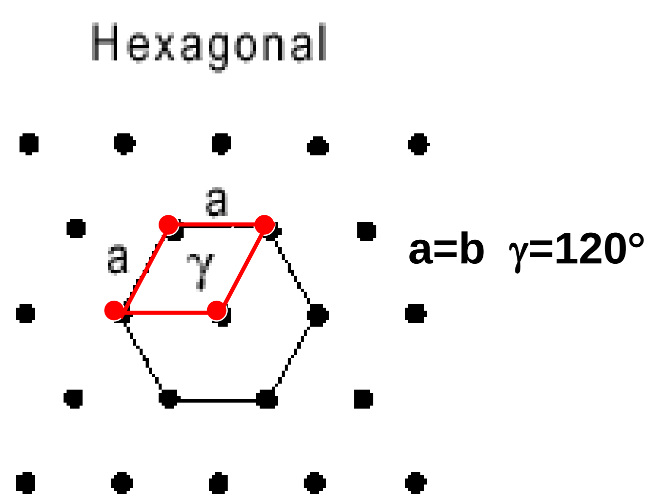


Unit Cell Choice

- There is always more than one possible choice of unit cell
- By convention the unit cell is chosen so that it is as small as possible while reflecting the full symmetry of the lattice

1) The highest symmetry
2) The smallest area (or volume)

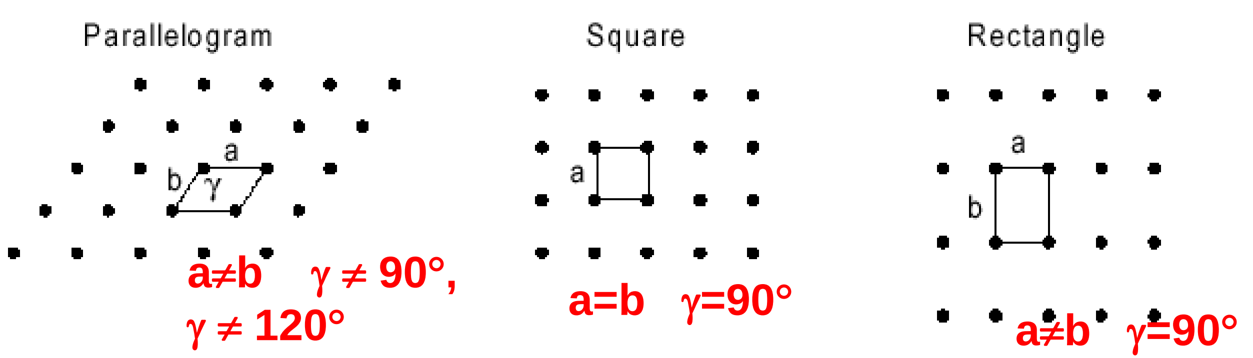
Five 2D lattices



$a=b$ $\gamma=120°$

Primitive unit cell

Five 2D lattices



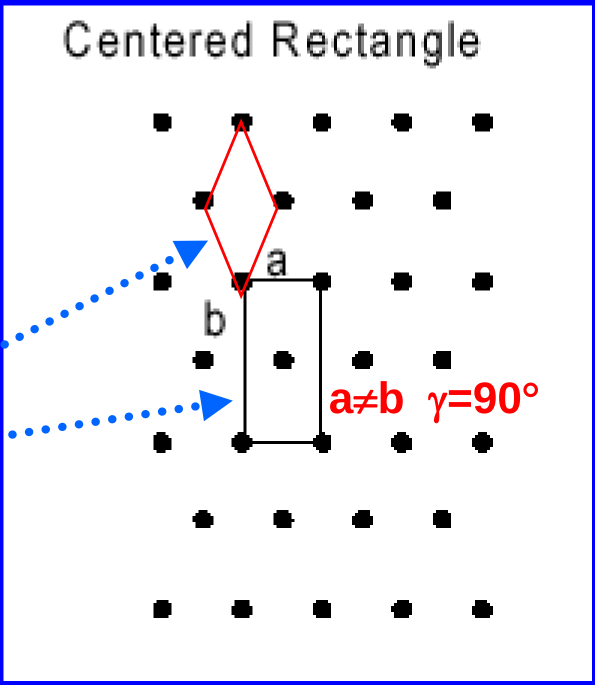
$a \neq b$ $\gamma \neq 90°$, $\gamma \neq 120°$

$a=b$ $\gamma=90°$

$a \neq b$ $\gamma=90°$

Primitive unit cell

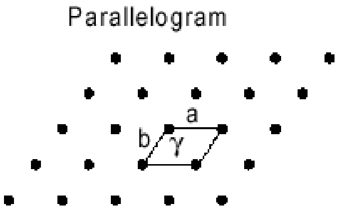
Five 2D lattices



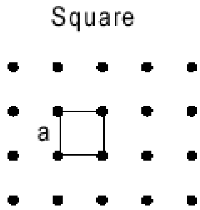
$a \neq b \quad \gamma = 90^\circ$

unit cell
Primitive
Centered

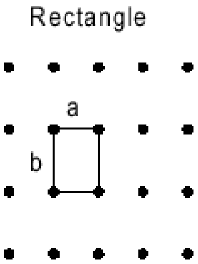
Five 2D lattices



$a \neq b \quad \gamma \neq 90^\circ,$
$\gamma \neq 120^\circ$

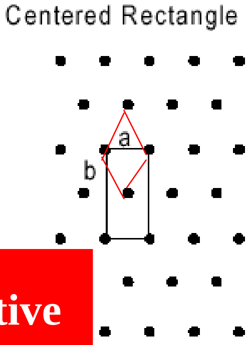


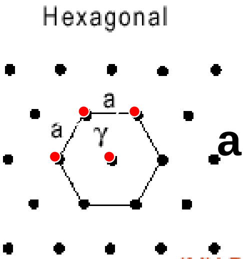
$a = b \quad \gamma = 90^\circ$



$a \neq b \quad \gamma = 90^\circ$

$a \neq b \quad \gamma = 90^\circ$



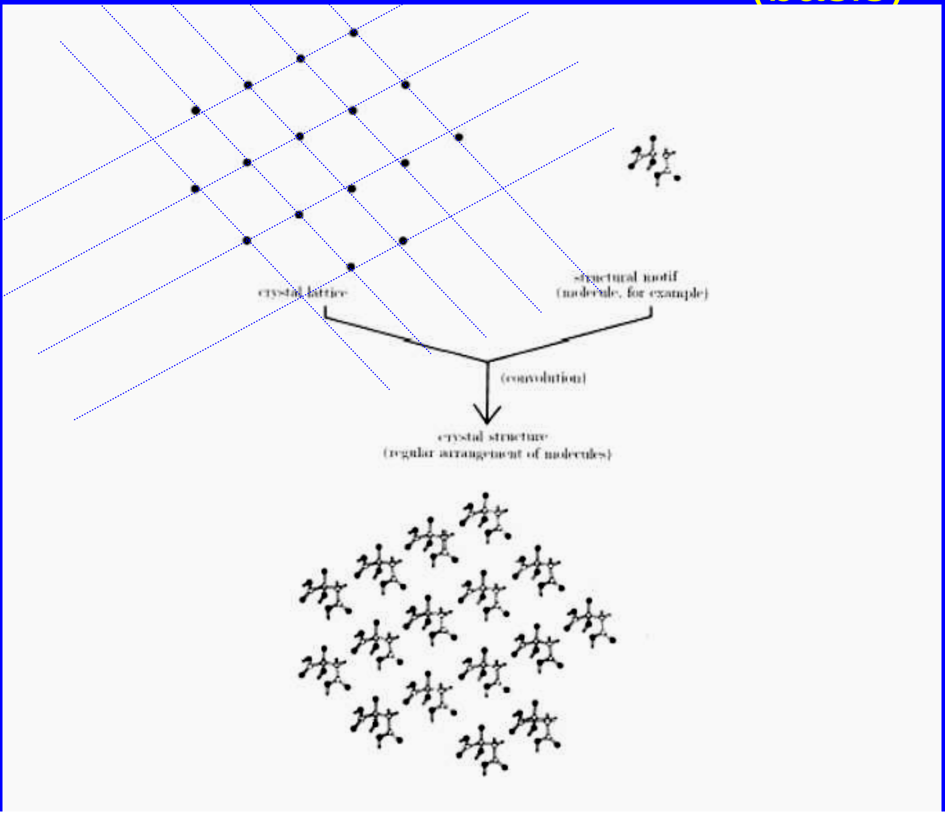


$a = b \quad \gamma = 120^\circ$

unit cell
Primitive
Centered

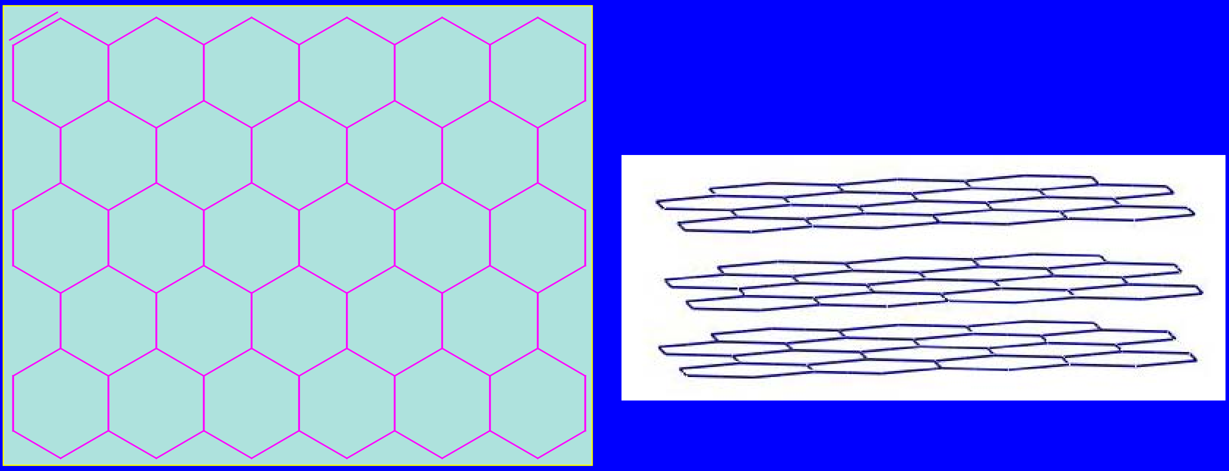
There are literally thousands of crystalline materials, there are only 5 distinct planar lattices

Crystal structure = lattice + structural motif (basis)

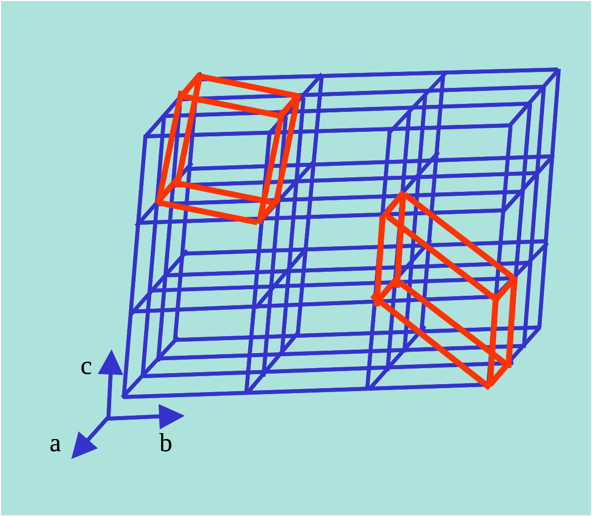


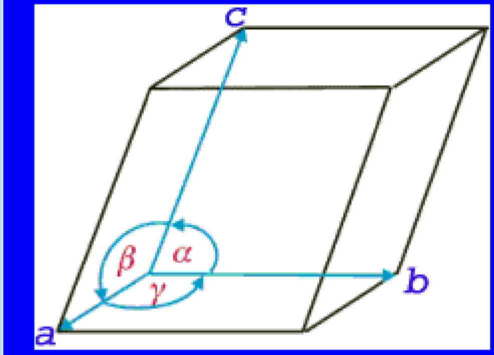
c. Lattices and its unit in 3D:

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

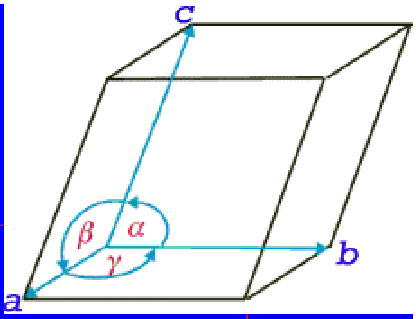


The Choice of a Unit Cell: Have maximum symmetry and minimum size





The Choice of a Primitive Cell

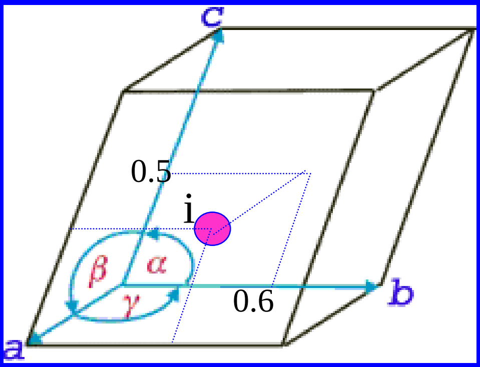


1) The axial system should be right handed
2) The basis vectors should coincide as much as possible with directions of highest symmetry
3) Should be the smallest volume that satisfies condition 2
4) Of all lattice vectors none is shorter than a
5) Of those not directed along a none is shorter than b
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

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:

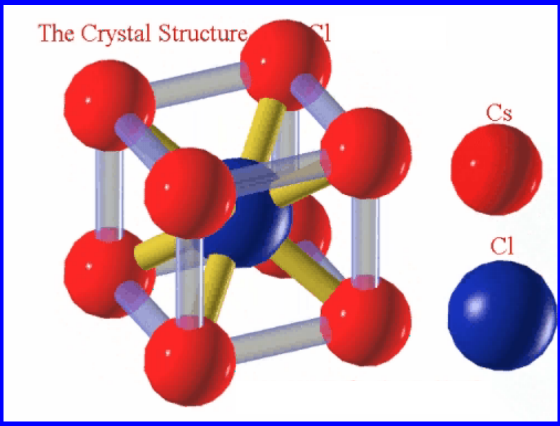
Cubic unit cell of CsCl,

a=b=c

α=β=γ=90°

Cs:(0,0,0)

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

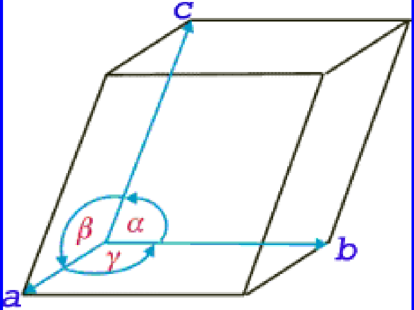


Single Crystal: Composed of only one particular type of space lattice.

Polycrystalline matter: Clusters of multiple crystals.

7.1.3 crystal systems and Bravais Lattices

a. crystal systems



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		$a \neq b \neq c$ $\alpha = \gamma = 90° \neq \beta$	b // 2-fold axis	C_{2h}
Orthorhombic		$a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$	a, b, c // 2-fold axes	D_{2h}
Trigonal	3-fold rotation axes	Rhombohedral $a = b = c$ $\alpha = \beta = \gamma < 120° \neq 90°$		D_{3d}
		Hexagonal $a = b \neq c$ $\alpha = \beta = 90°$ $\gamma = 120°$		D_{6h}
Tetragonal	4-fold rotation axes	$a = b \neq c$ $\alpha = \beta = \gamma = 90°$	c // 4-fold axis	D_{4h}
Hexagonal	6-fold rotation axes	$a = b \neq c$ $\alpha = \beta = 90°$ $\gamma = 120°$	c // 6-fold axis	D_{6h}
Cubic	Four 3-fold rotation axes	$a = b = c$ $\alpha = \beta = \gamma = 90°$	Four 3-fold axes are parallel to the four body diagonals of the cube	O_h

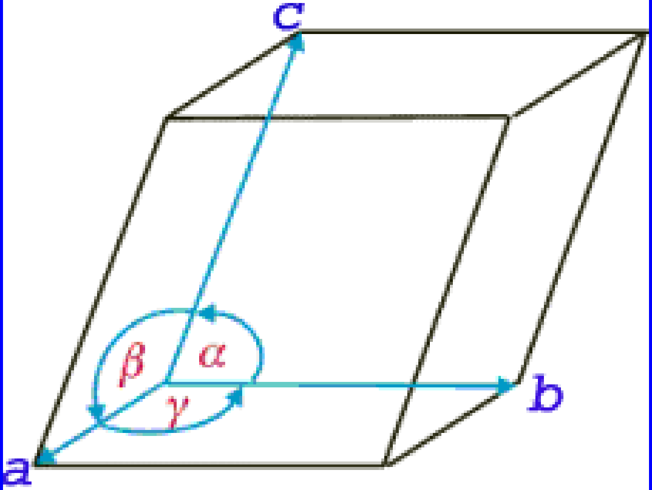
b. Bravais Lattice: (14)

Unit Cell: have maximum symmetry and minimum size

*** Triclinic**

a≠b≠c

α≠β≠γ

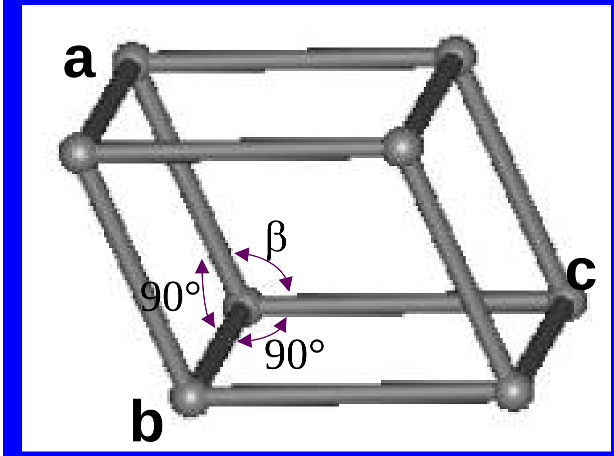


P (Primitive)

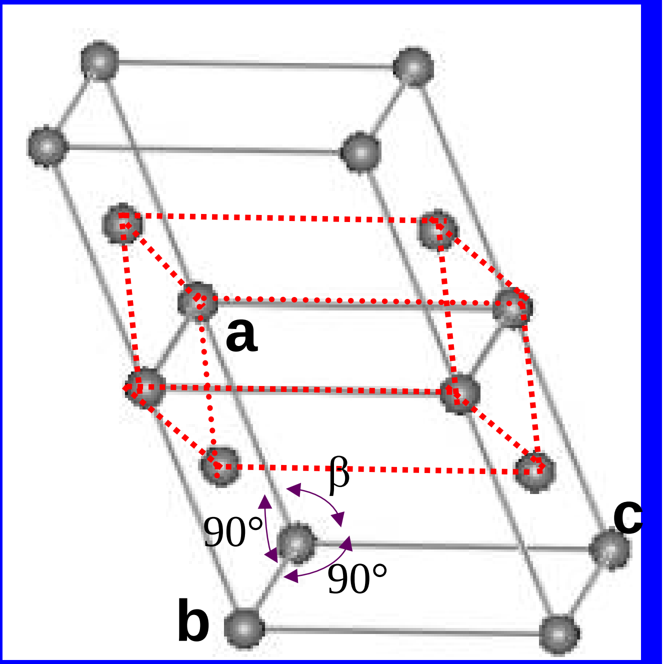
*** Monoclinic**

a≠b≠c

α= γ =90º ≠β



P (Primitive)



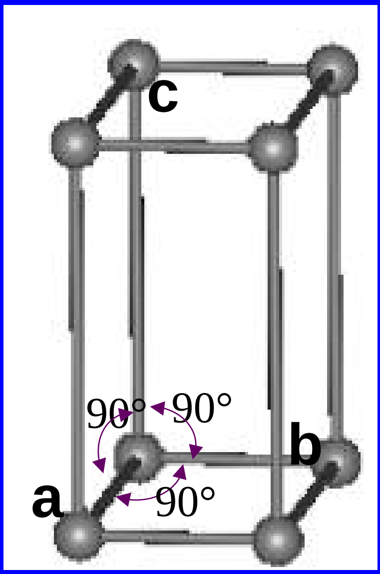
C-centered or A-centered

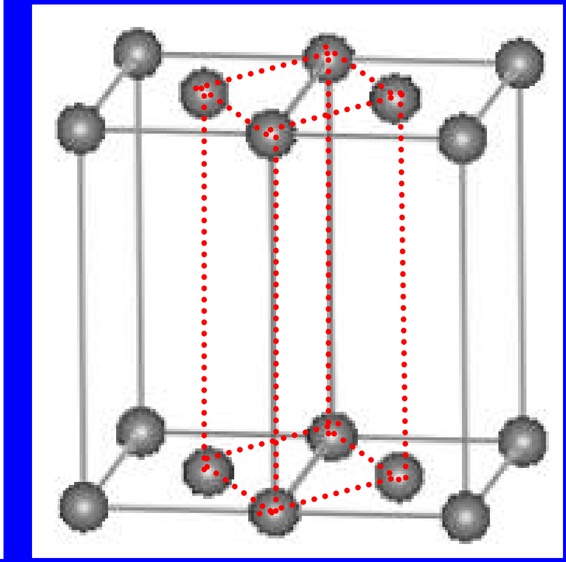
A primitive unit cell contains one lattice point and a C-centered unit cell contains two lattice points.

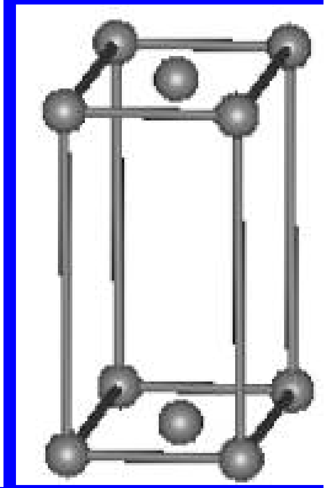
* Orthorhombic

$a \neq b \neq c$

$\alpha = \beta = \gamma = 90^\circ$







P (Primitive) C-centered or A-centered or B-centered

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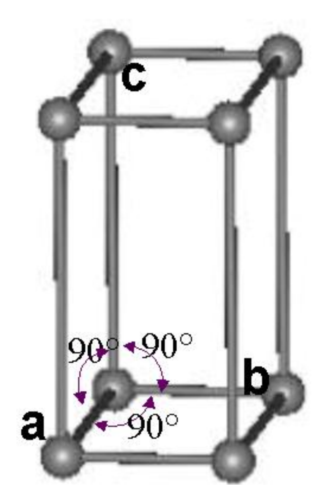
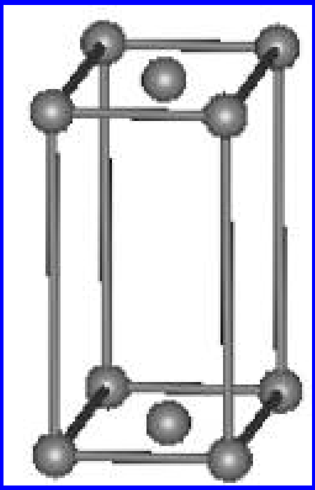
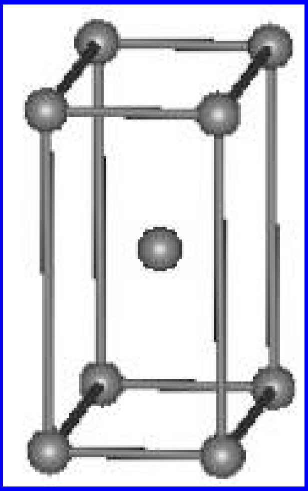
* Orthorhombic

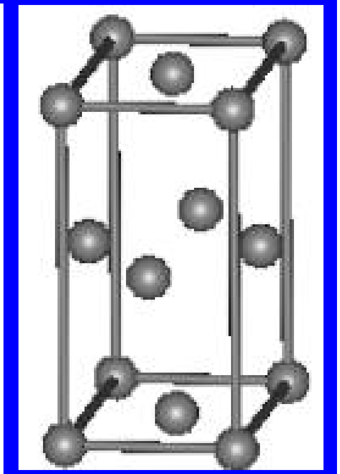
$a \neq b \neq c$

$\alpha = \beta = \gamma = 90^\circ$



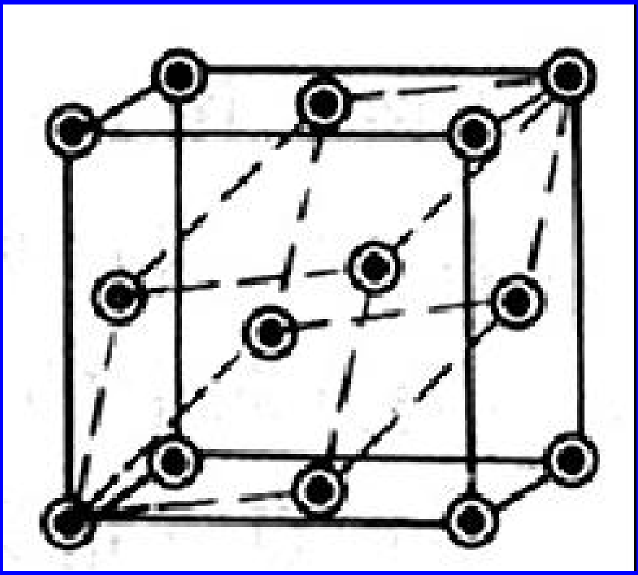






P C or A or B I (In-centered) F (Face-centered)

Face-centered cell and its primitive cell



A Face-centered unit cell contains four lattice points.

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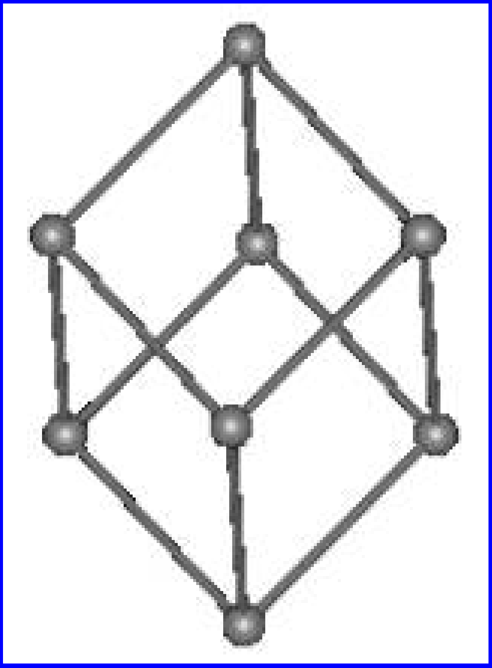
* Trigonal ---- **Rhombohedral**

a=b=c

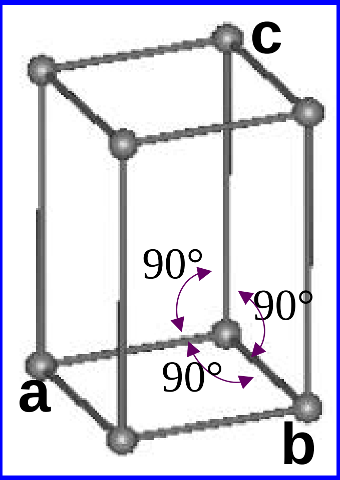
$\alpha = \beta = \gamma \neq 90^{\circ}$



* Tetragonal

a=b≠c

α= β =γ =90º



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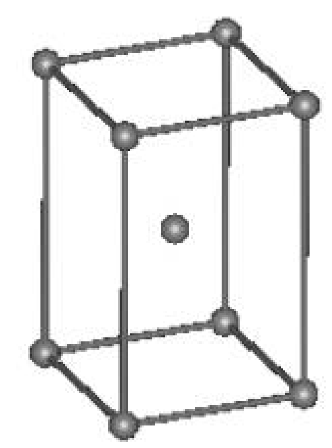

I

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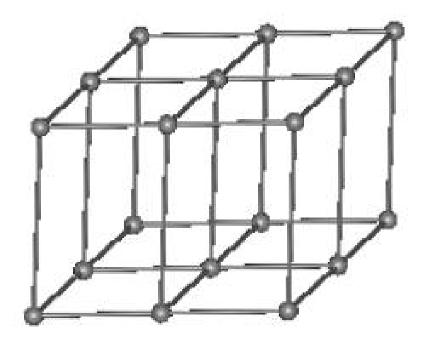
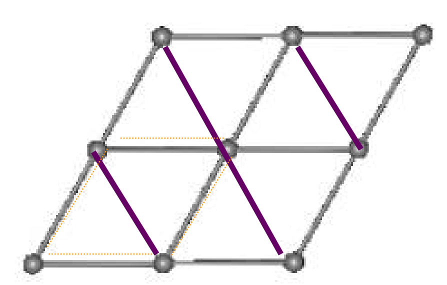
* Hexaagonal

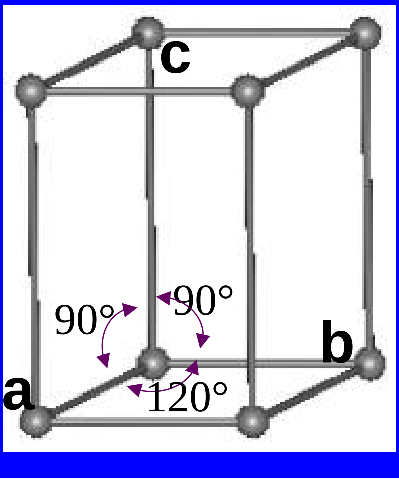
a=b≠c

α= β =90º,
γ =120º





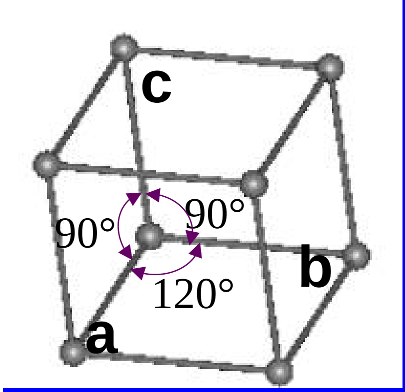
Unit cell



*** Cubic**

a=b=c

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



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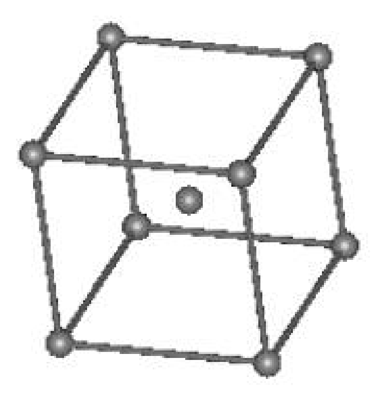

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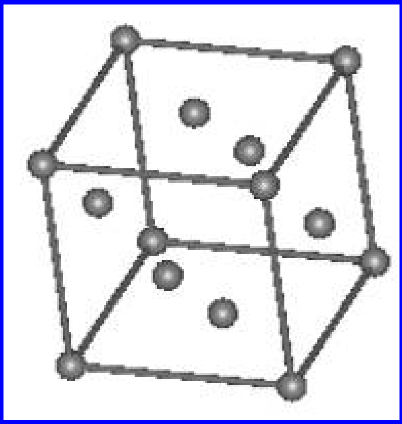

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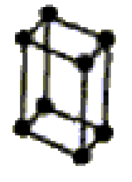
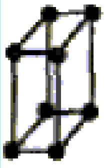
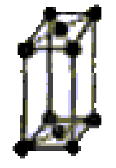
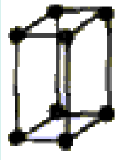
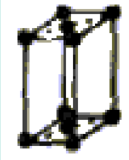
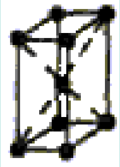
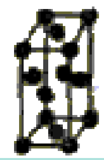
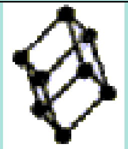
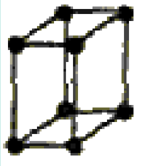
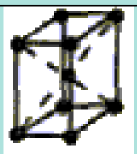
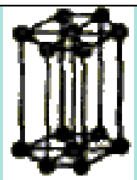
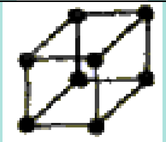
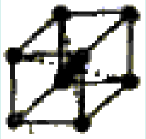
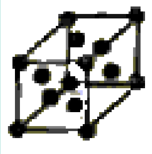
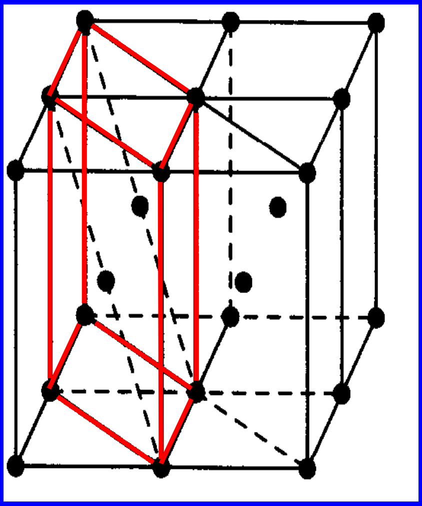
b. Bravais Lattice: (14)

Unit Cell: have maximum symmetry and minimum size

Centred Unit cell:

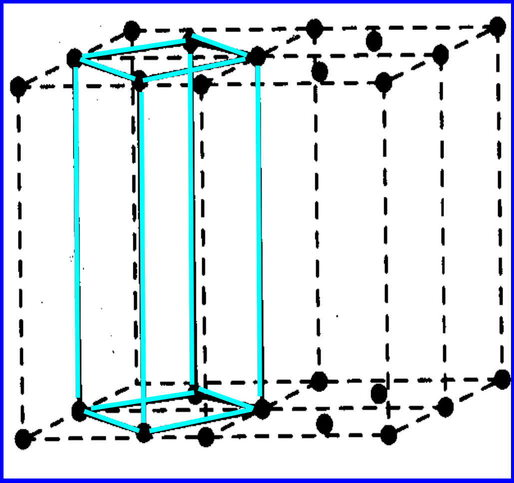
Crystal systems	P	C	I	F
Triclinic				
Monoclinic				

Orthorhombic				
Trigonal				
Tetragonal				
Hexagonal				
Cubic				



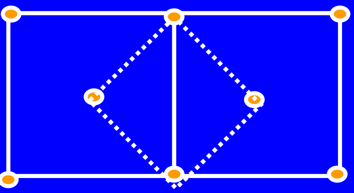
Monoclinic

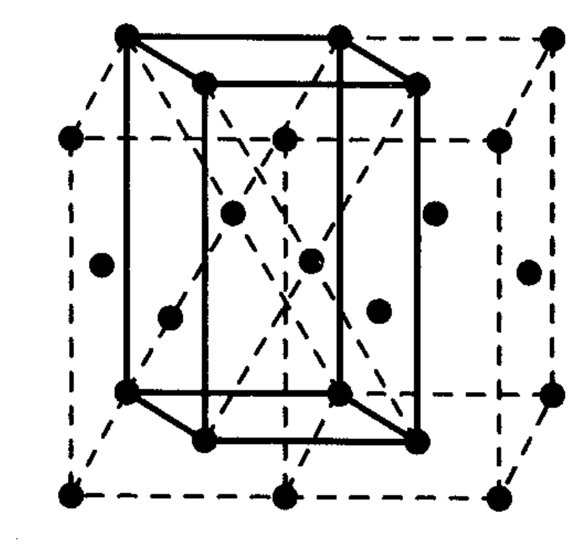
I = C



Tetragonal

C = P



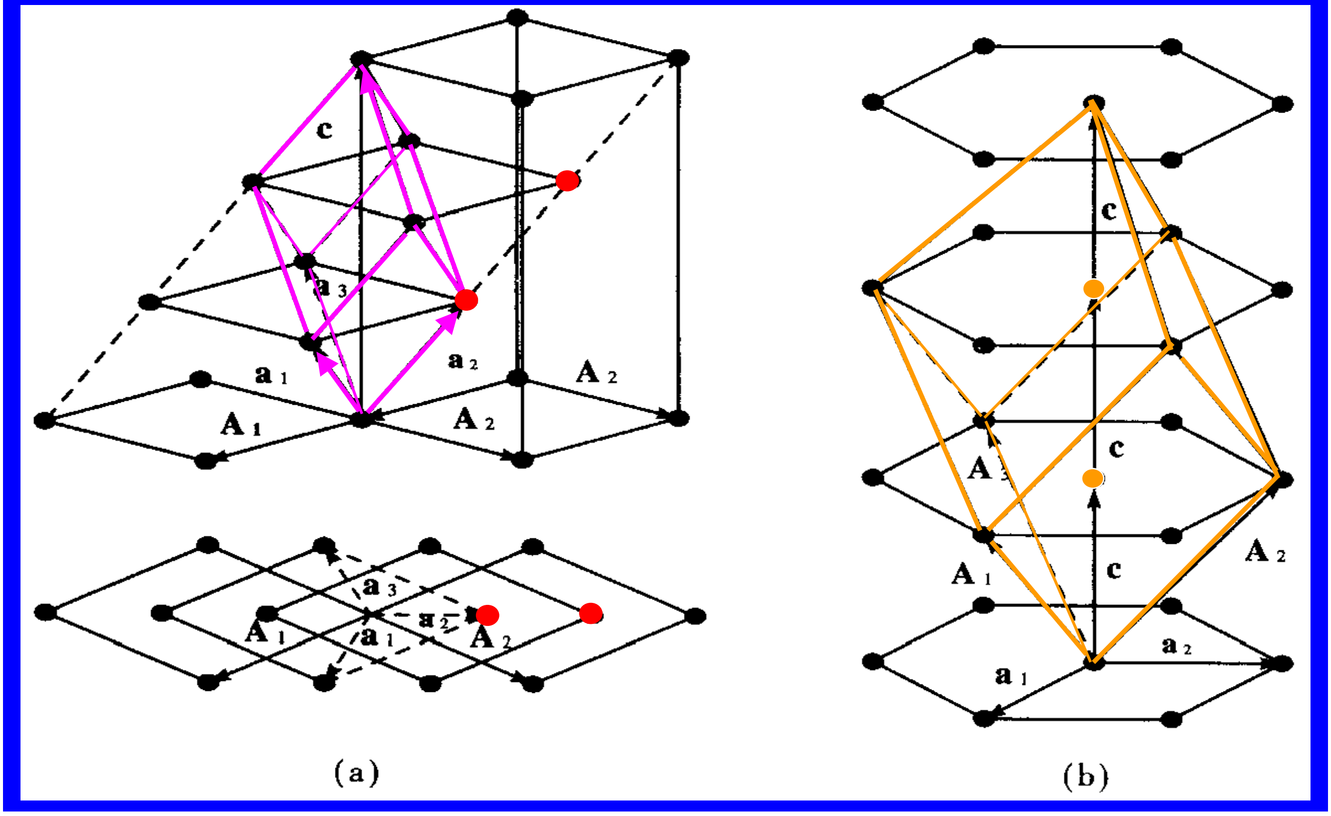


Monoclinic F = C

---

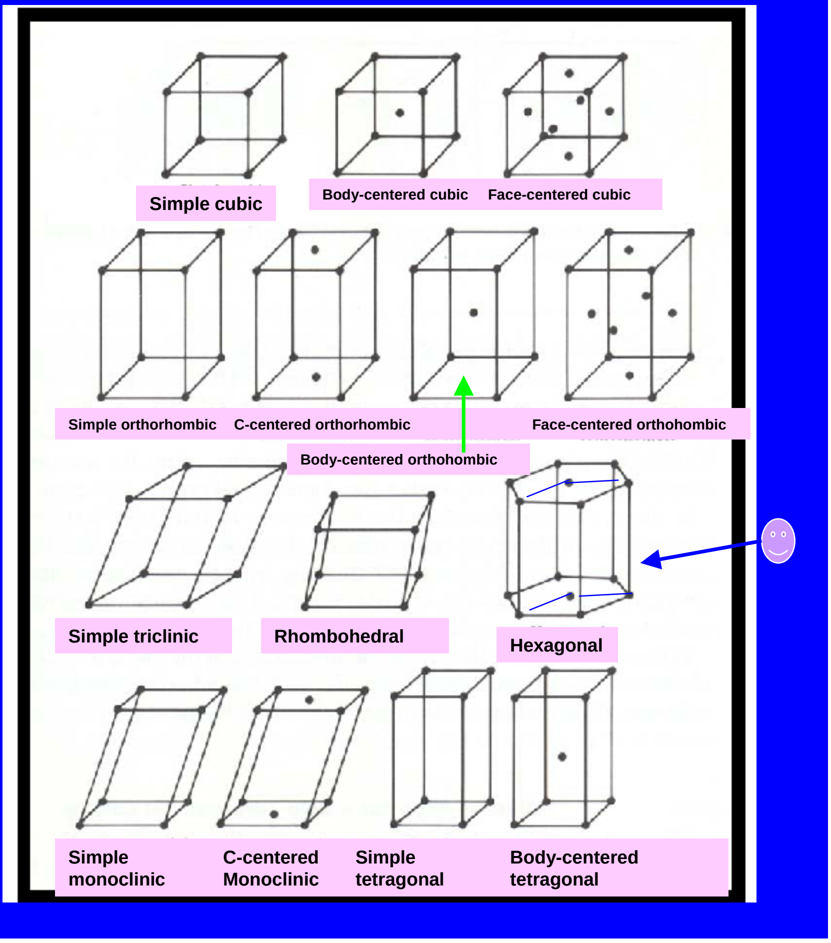
a.Primitive rhomohedral-
r-centered hexagonal

b.primitive hexagonal
r-centered rhombohedral



Bravais Lattices

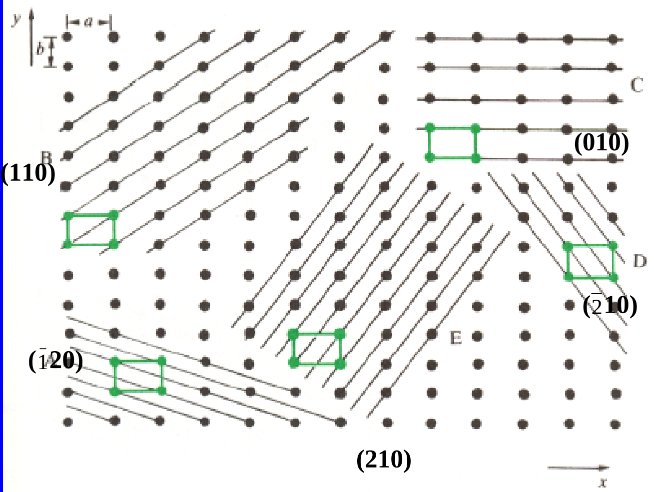
Died 30 Mar 1863 (born 23 Aug 1811)
French physicist best remembered for his work on the lattice theory of crystals; Bravais lattices are named for him.



7.1.4 Crystal Planes and Miller Indices

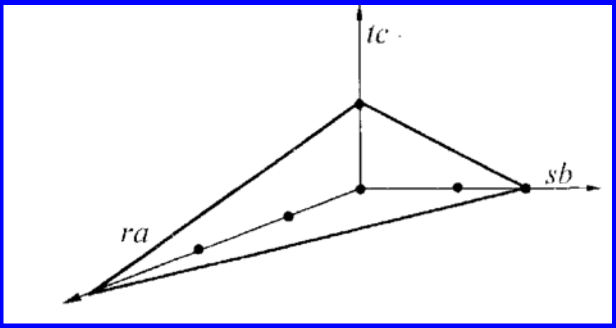
a.Lattice planes

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)

Miller indices are the reciprocal intercepts of the plane on the unit cell axes.

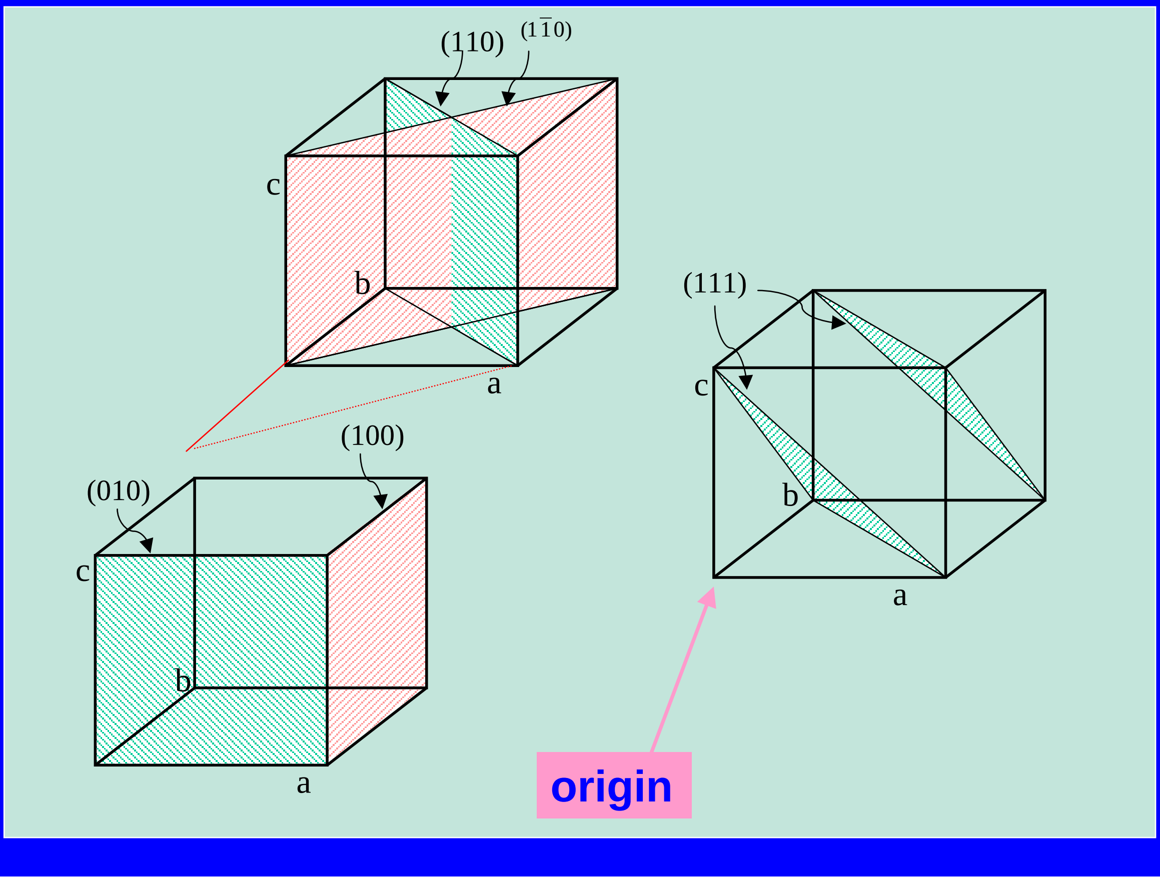


$$\frac{1}{r}:\frac{1}{s}:\frac{1}{t}=h:k:l$$

Example: 1/3:1/2:1/1 = 2:3:6

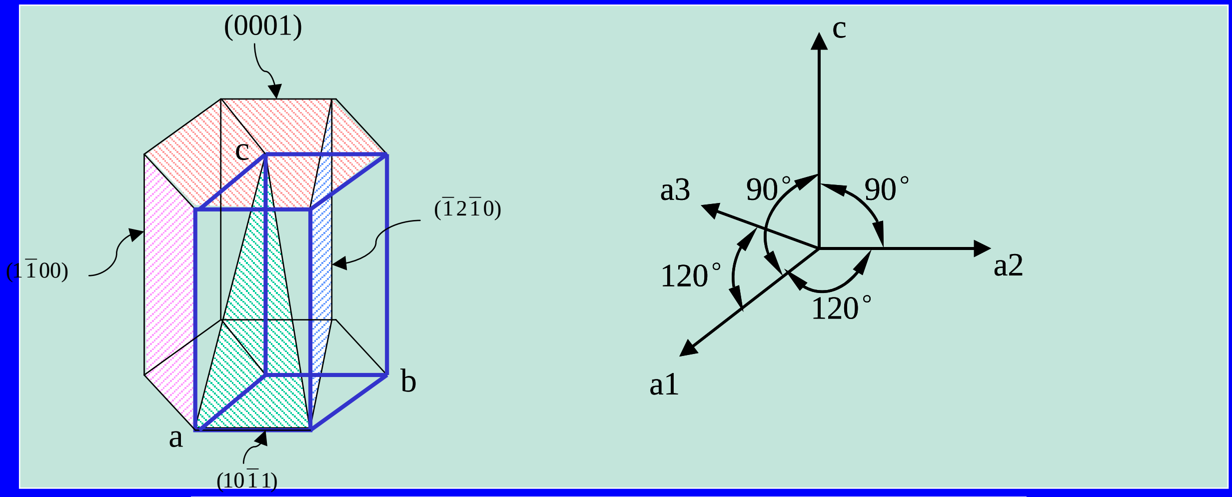
The Miller index is (236)

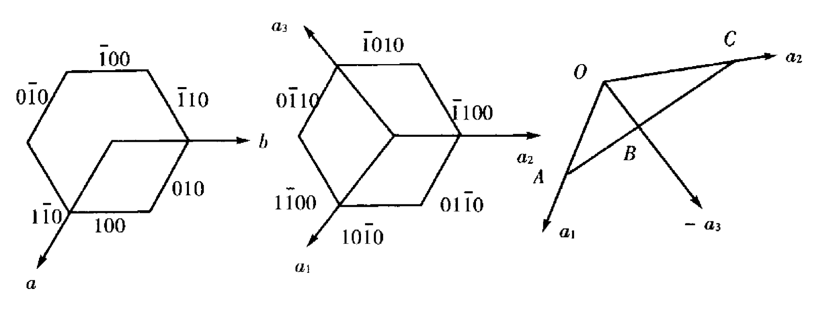
Examples of Miller indices



hexagonal, four axis (a1,a2,a3,c)

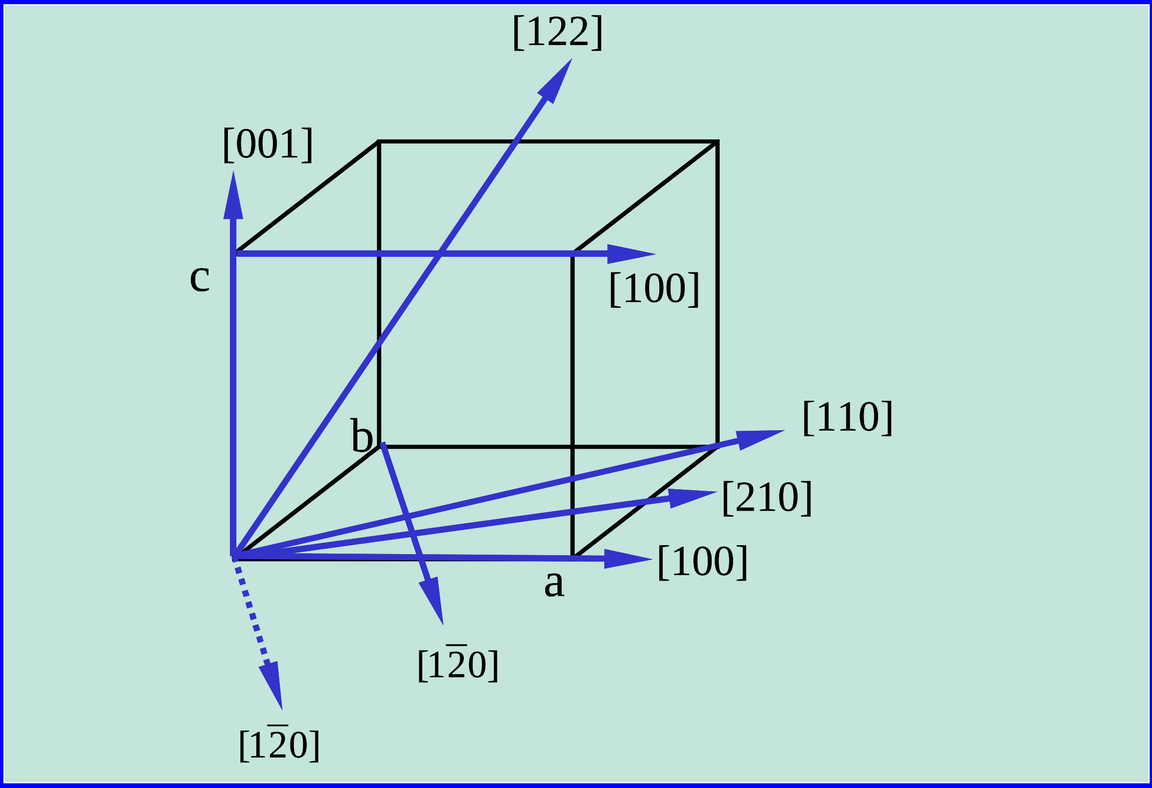
(hkil), i=-(h+k)



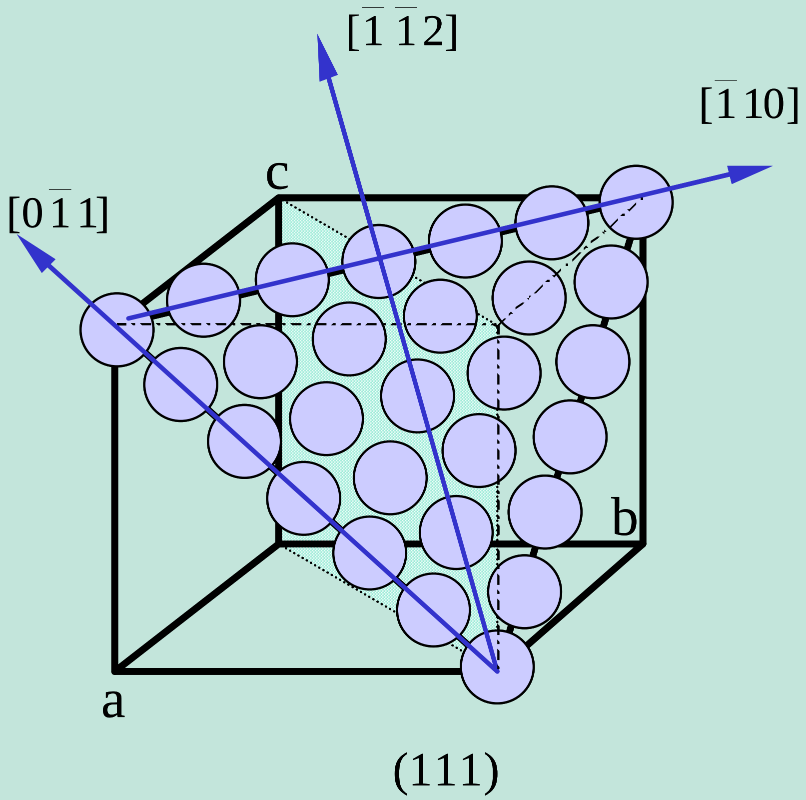


hexagonal, four axis (a1,a2,-(a1+a2),c)

C. Directions in lattice



Example: Directions on the (111) plane.



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

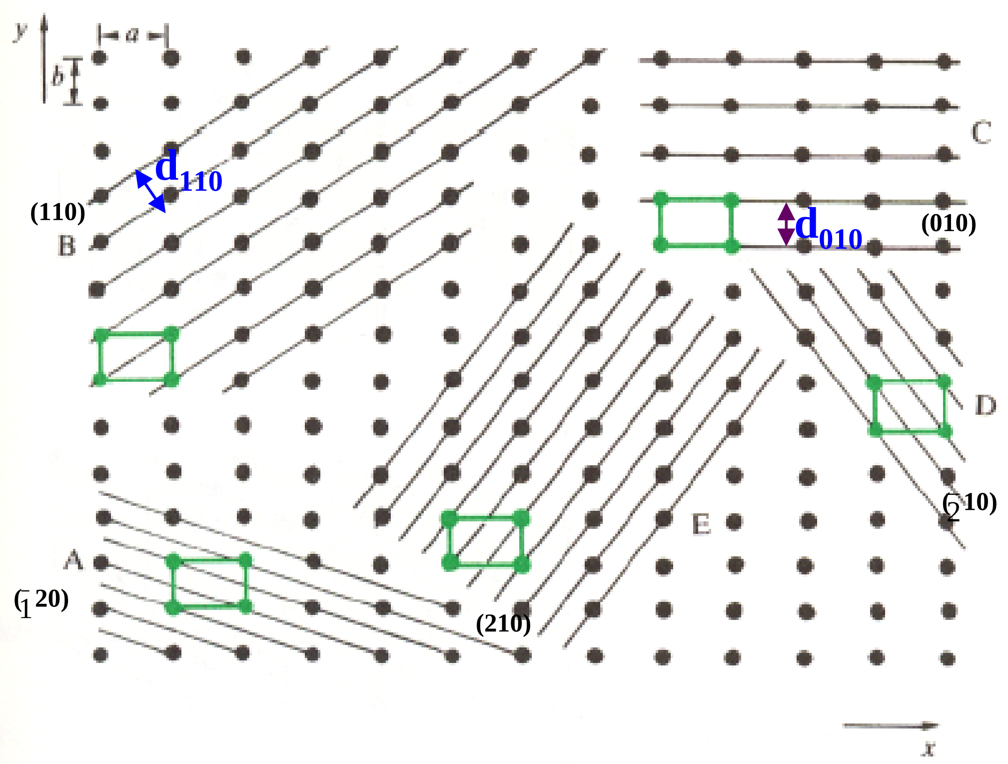
{hkl} are used to specify all symmetry equivalent sets of planes

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.

[uvw] zone axis

d. d-spacing d_{hkl}

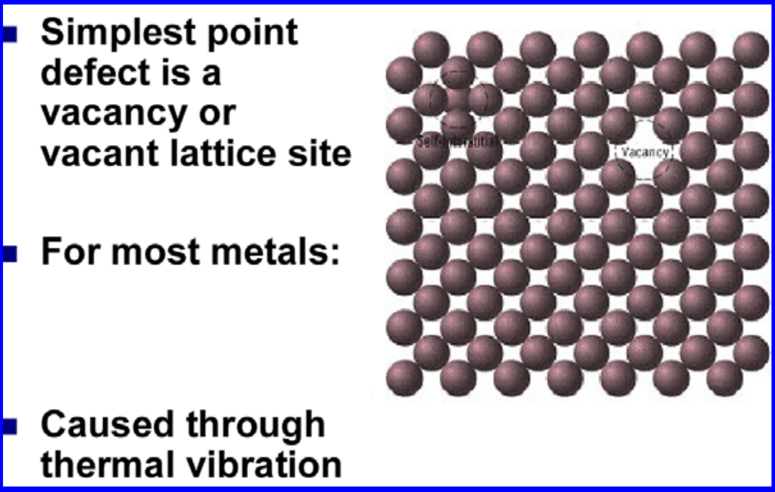


The spacing between adjacent planes in a family is referred to as a "d-spacing"

- **Cubic :** $1/d^2 = (h^2+k^2+l^2)/a^2$
- **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:**

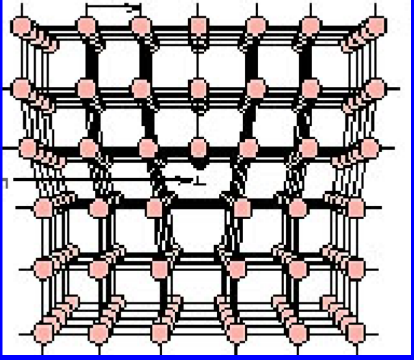
7.1.5 Real crystals and Crystal defects：

Real crystals are only close approximations of space lattices



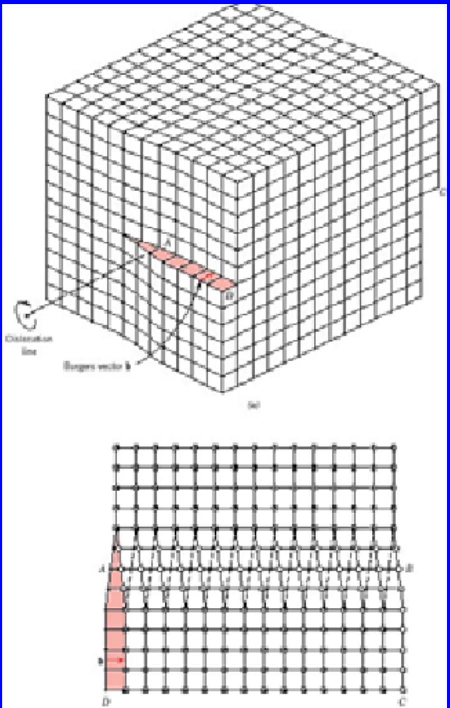
- Simplest point defect is a vacancy or vacant lattice site
- For most metals:
- Caused through thermal vibration

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 in a crystal to minimize the number of independent coordinates**

a. Lattice symmetry

b. Point symmetry

c. Other translational symmetry elements: screw axes and glide planes

a. Lattice symmetry --- translation operation

T_{mnp}=ma+nb+pc

$$T_{mnp} = \begin{bmatrix} m \\ n \\ p \end{bmatrix}$$

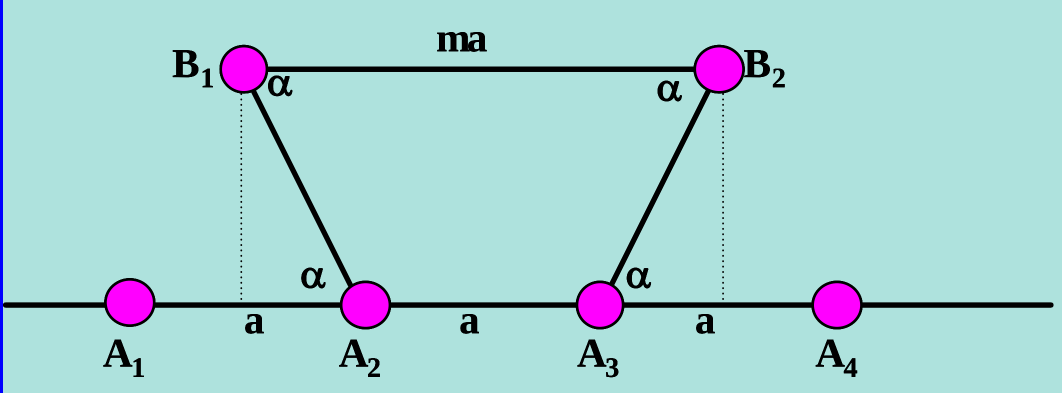
b. Point symmetry elements compatible with 3D translations

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

- Point symmetry operation does not alter at least one point that it operates on: rotation axes, mirror planes, rotation-inversion axes

---

Rotation axes, 1,2,3,4,6 only!! Why ???



Lattice points A_1, A_2, A_3, A_4

Through n-fold operation

$A_1 \longrightarrow B_1$

$A_4 \longrightarrow B_2$

$A_1A_4 \parallel B_1B_2$

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

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

$|(m-1)/2| \leq 1$

$|m-1| \leq 2$

m = 3, 2, 1, 0, -1

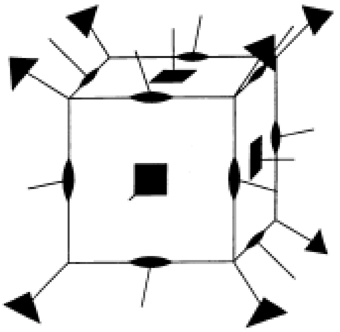
cos α=1, 1/2, 0, -1/2, -1

α = 0°, 60°, 90°, 120°, 180°

n= 1, 6, 4, 3, 2

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

The symmetry elements of a cube

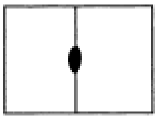


⬬ **Twofold axis**

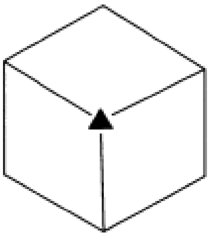
▲ **Threefold axis**

■ **Fourfold axis**

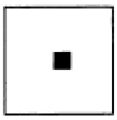
2 3 4 6
Rotation axis



twofold axis



threefold axis



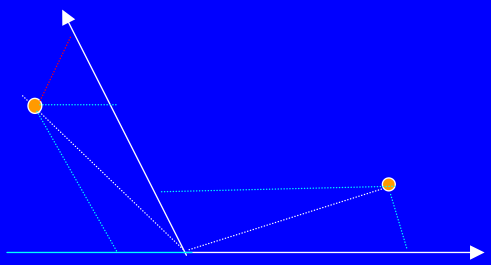
fourfold axis

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

general equivalent positions:
(x,y,z); (-x, y, -z)

2 fold axis // b

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



general equivalent positions:
(x,y,z), (-y, x-y, z) (-x+y, -x, z)

3 fold axis // c

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

general equivalent positions: (x,y,z), (-y, -x, z), (-x,-y,z), (y,-x,z)

4 fold axis // c

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

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)

6 fold axis // c

---

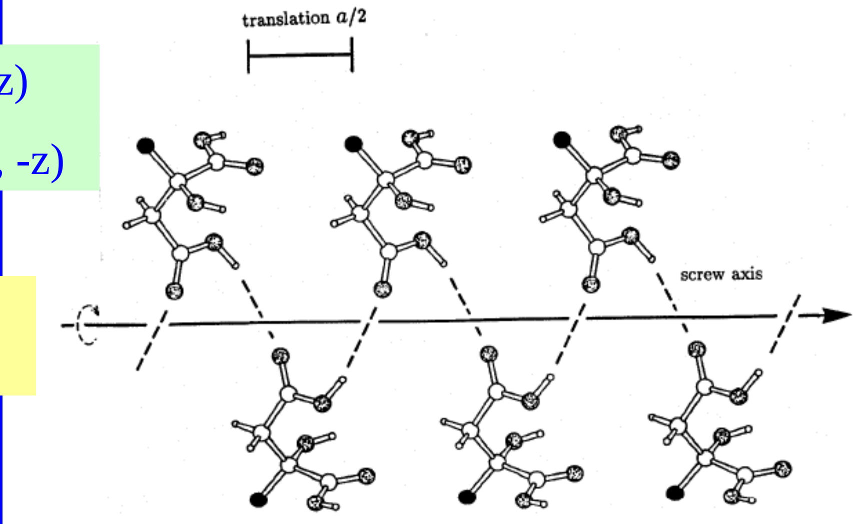
c.Screw axes and glide planes:

A two-fold screw 2_1

(x,y,z)→(x, –y, -z)

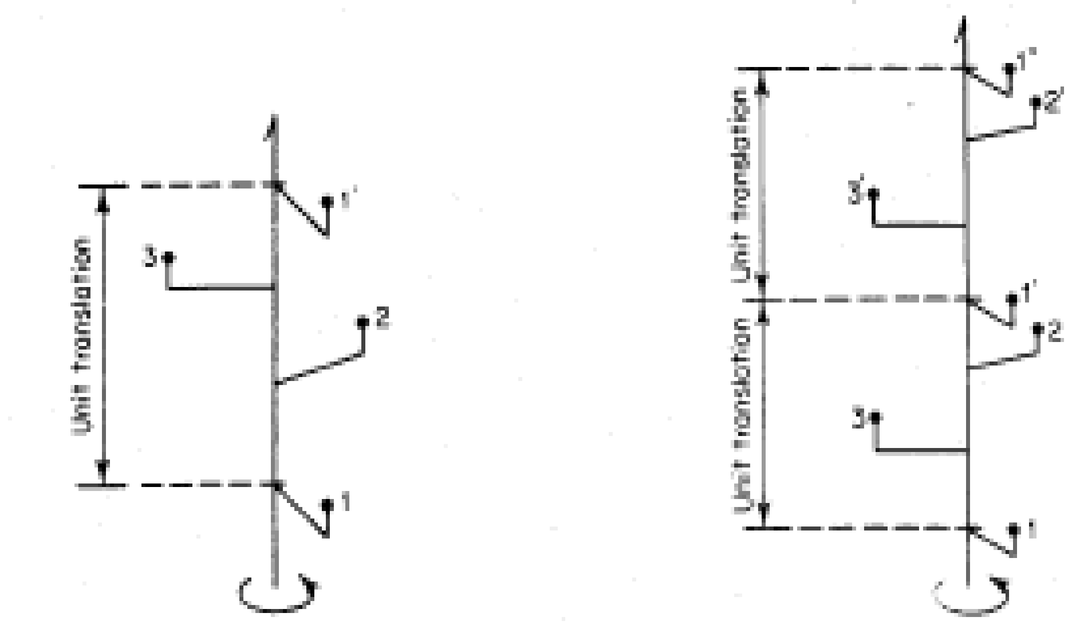
→(x+1/2,-y, -z)

Helical structure



The direction of such an axis is usually along a unit cell edge, and the translation must be a subintegral fraction of the unit translation in that direction.

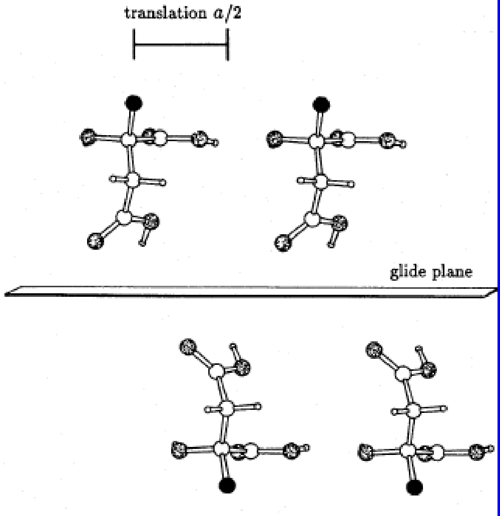
Higher order screw axes



Screw 3_1

Screw 3_2

An *a* glide



$(xyz) \rightarrow (-x\ y\ z)$

$\rightarrow (-x+1/2\ \ y\ \ z)$

Zig-zag structure

Other glide operations

- a, b, c, n and d glides occur
- a glide has translational component of 1/2a
- n glide has trandlational component 1/2a+1/b or 1/2b+1/2c or …
- d glide has translational component of the type 1/4a+1/4b+1/4c
- e glide

Summary of symmetry elements and symmetry operations in crystal structure

Rotation operation	rotation axis
Reflection operation	mirror plane
Inversion operation	center of symmetry
Rotation inversion operation	inversion axis
Translation operation	lattice
Screw operation	screw axis
Glide operation	glide plane

n=1, 2, 3, 4, 6

7.2.2 Space group and point group

Space group: 230

Schonflies notation and International notation

D_{2h}^{16} - $P2_1/n\ 2_1/m\ 2_1/a$ C_{2h}^{5} – $P2_1/c$

system	directions		
	1	2	3
Cubic	**a**	**a+b+c**	**a+b**
hexagonal	**c**	**a**	**2a+b**
Tetragonal	**c**	**a**	**a+b**
Trigonal	**a+b+c**	**a-b**	**-**
Trigonal*	**c**	**a**	
Orthorhombic	**a**	**b**	**c**
monoclinic	**b**	**-**	**-**

C_{2h}^5 – $P2_1/c$

General equivalent positions:

4 1 e (1) x,y,z; (2) -x, 1/2+y, 1/2-z; (3)x, 1/2-y, 1/2+z;(4) -x,-y,-z

Special equivalent positions

2 d 1bar 1/2,0, 1/2; 1/2, 1/2, 0

2 c 1bar 0,0, 1/2; 0, 1/2, 0

2 b 1bar 1/2,0,0; 1/2, 1/2, 1/2

2 a 1bar 0,0,0; 0, 1/2, 1/2

International tables for crystallography

$P2_1/c$~20%

efficiency packing

Combining symmetry elements

When a crystal possesses more than one of the above 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 and these are the 32 crystallographic point groups.

32 point groups

14 Bravais lattices

7 Crystal systems

but only 230 space groups

7.2.3 The description and application of crystal structure

Example 1. Crystal of iodine

Crystal System orthorhombic

Space group D^{18}_{2h}-Cmca

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

Equivalent positions: (0,0,0)+, (1/2, 1/2, 0)+,

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)

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

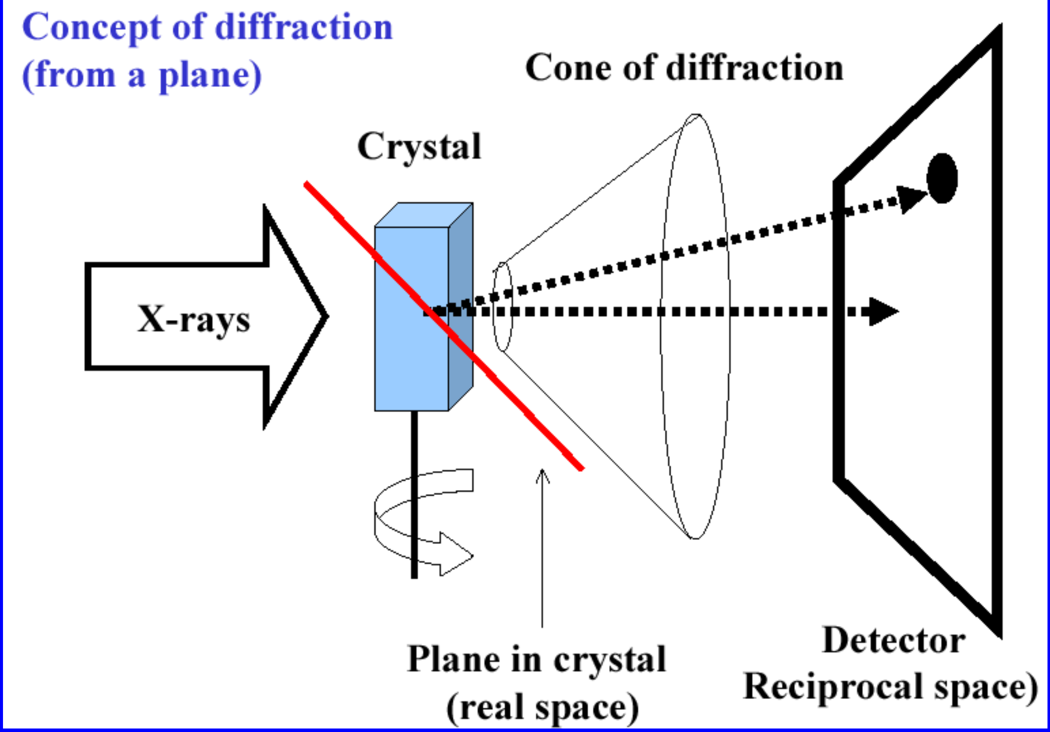
c) Density of crystal

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

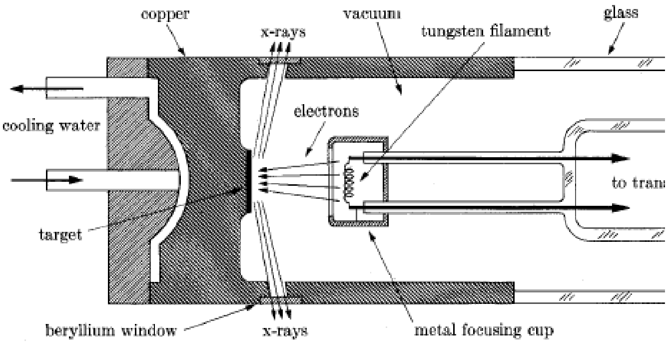
$D = 8 \times 127.0 /(6.02 \times 10^{23} \times 327.0 \times 10^{-24})$ g cm^{-3}

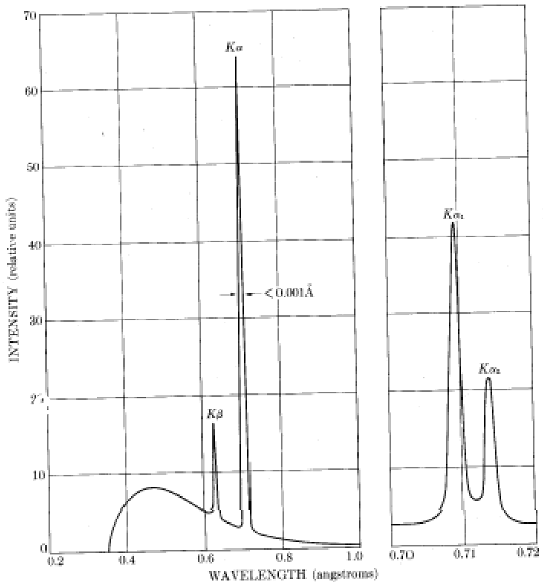
=5.16 g cm^{-3}

7.3 X-ray diffraction of crystals



7.3.1 The source and property of X-ray



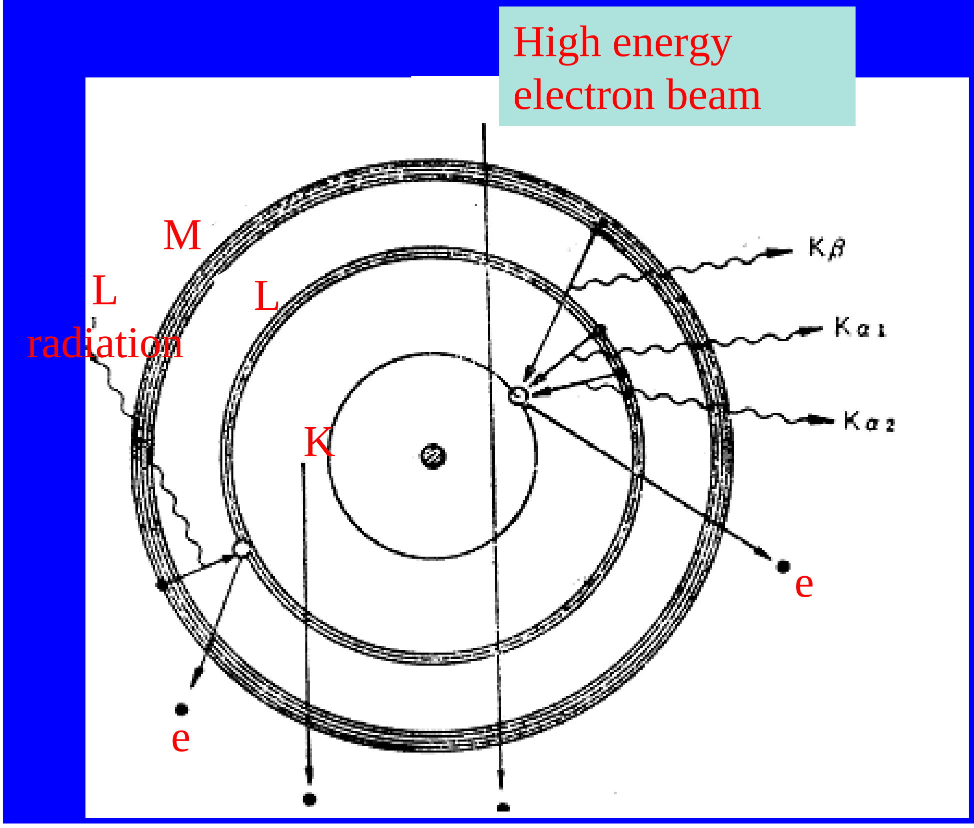


X-ray tube

the wavelengths of X-ray are in the ra
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



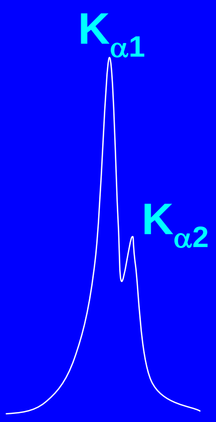
As for Cu:

$K_{\alpha 1}=1.540594\text{Å}$

1.54056Å

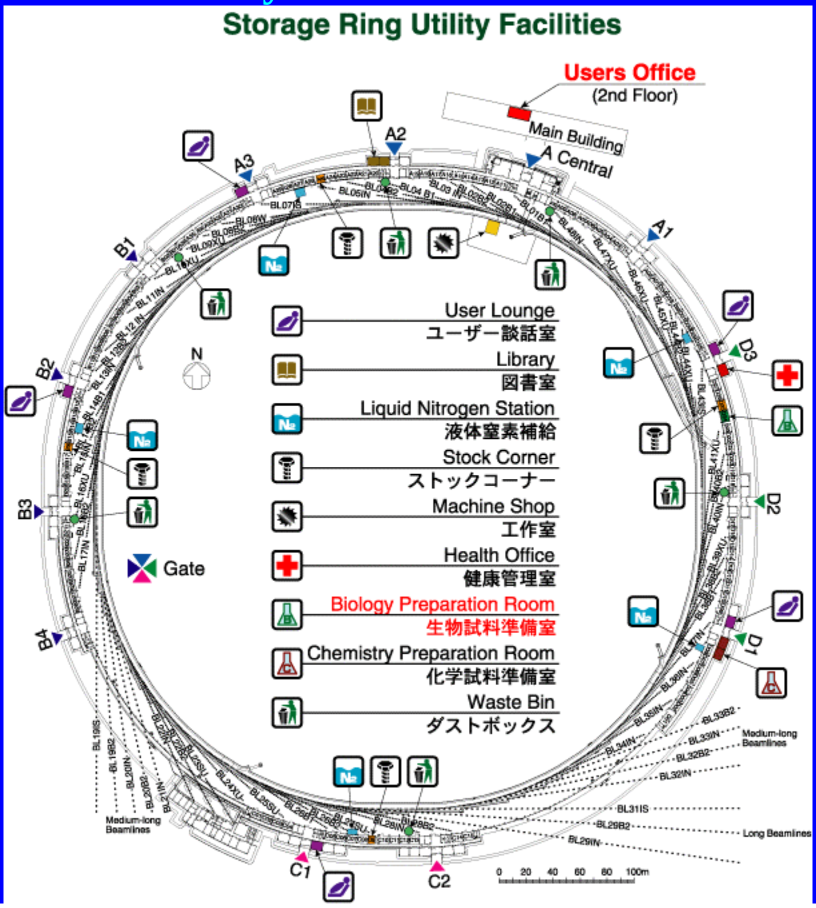
$K_{\alpha 2}=1.544422\text{Å}$

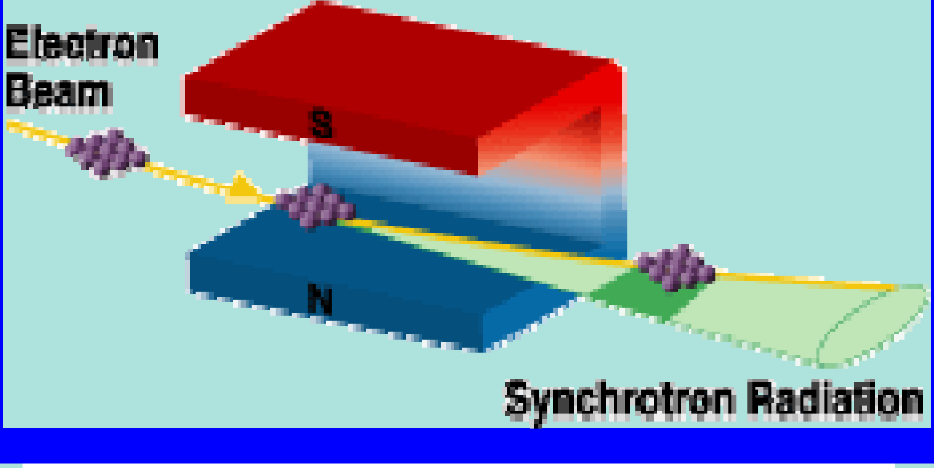
$I_{K\alpha 1} \approx 2I_{K\alpha 2}$

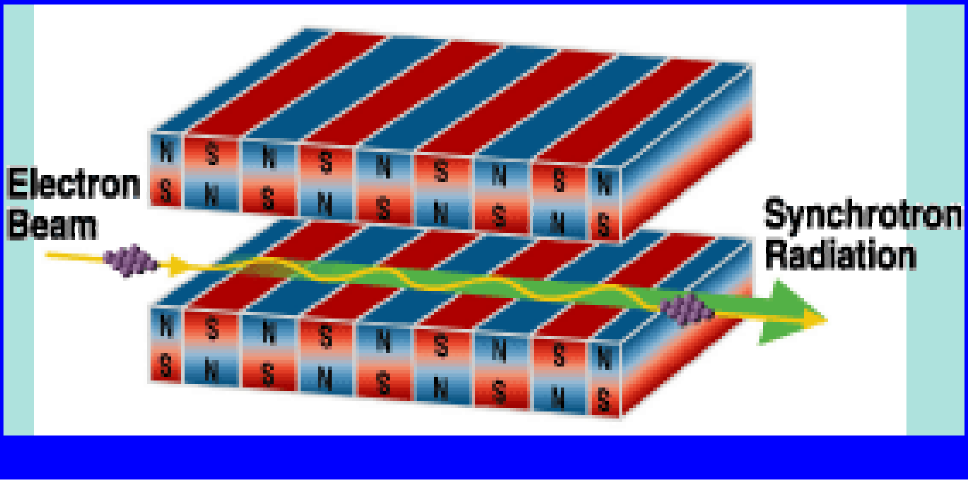


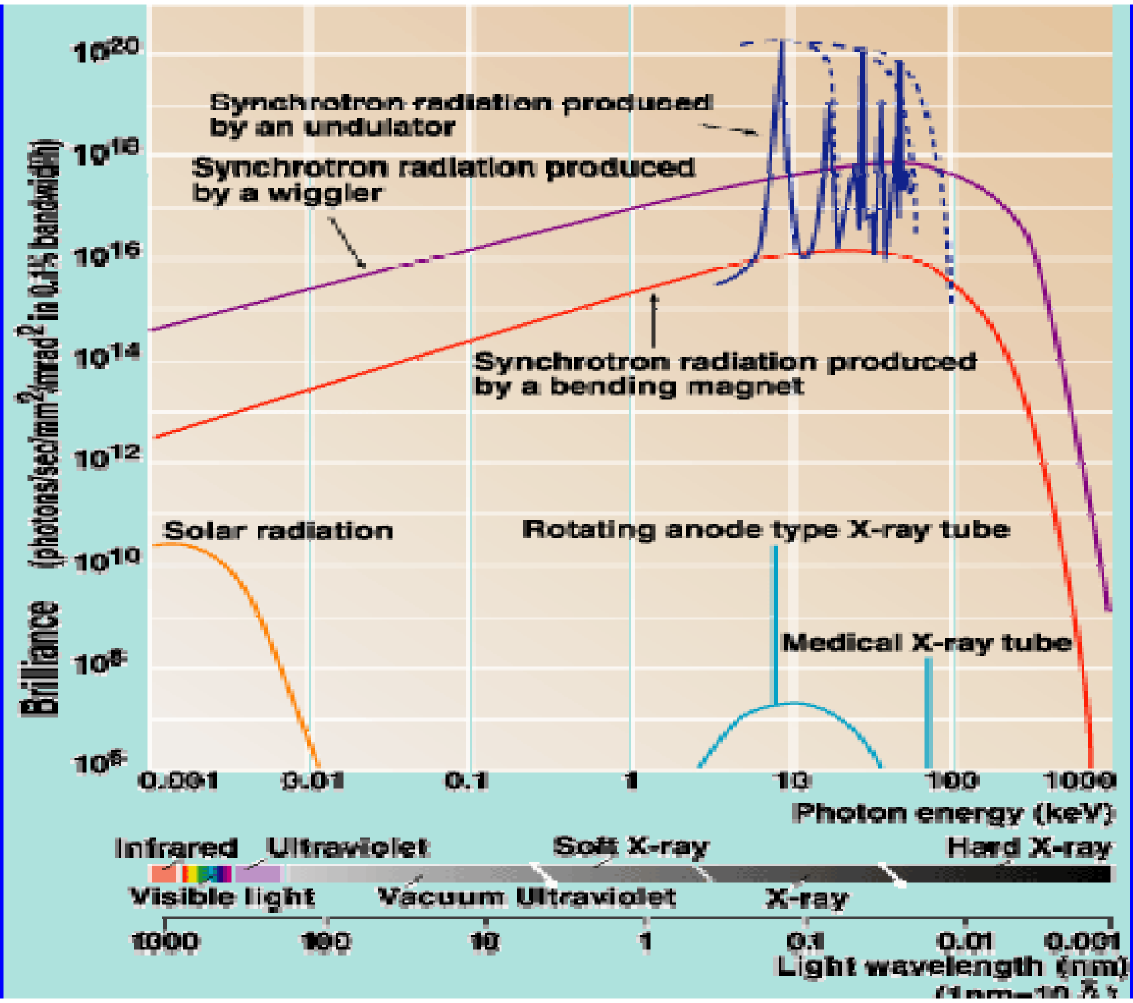
Notice: $K_{\alpha 2}$ can not be striped by the monochromator.

Synchrotron Radiation X ray Source








Brilliance (photons/sec/mm^2/mrad^2 in 0.1% bandwidth)
10^{20}
10^{18}
10^{16}
10^{14}
10^{12}
10^{10}
10^{8}
10^{6}
Synchrotron radiation produced by an undulator
Synchrotron radiation produced by a wiggler
Synchrotron radiation produced by a bending magnet
Solar radiation
Rotating anode type X-ray tube
Medical X-ray tube
0.001
0.01
0.1
1
10
100
1000
Photon energy (keV)
Infrared
Ultraviolet
Soft X-ray
Hard X-ray
Visible light
Vacuum Ultraviolet
X-ray
1000
100
10
1
0.1
0.01
0.001
Light wavelength (nm)
(1nm=10 Å)


HASYLAB
SRS
Super ACO
BESSY
ESRF
ELETTRA
SSRC
CAT
BSRF
PLS
NSRL
PF
SPring-8
SRRC
ALS
SSRL
SRC
CHESS
APS
NSLS
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

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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

The Nobel Prize in Physics 1914
"for his discovery of the diffraction of X-rays by crystals"

The derivation of the Laue equation

Interference condition:

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

AD-CB = $\boldsymbol{a}\cdot\boldsymbol{s}-\boldsymbol{a}\cdot\boldsymbol{s}_0$ =

$$\boldsymbol{a}\cdot(\boldsymbol{s}-\boldsymbol{s}_0) = h\lambda$$

Or,

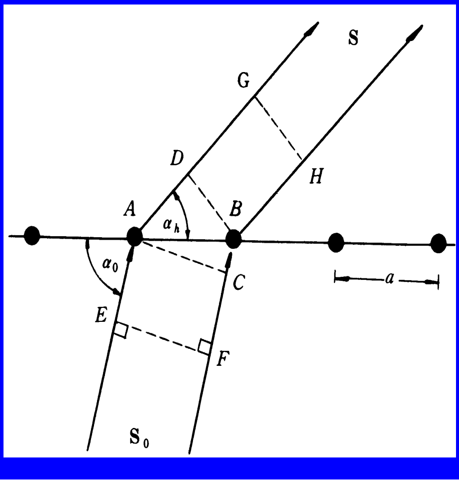
$$a(\cos\alpha - \cos\alpha_0) = h\lambda$$

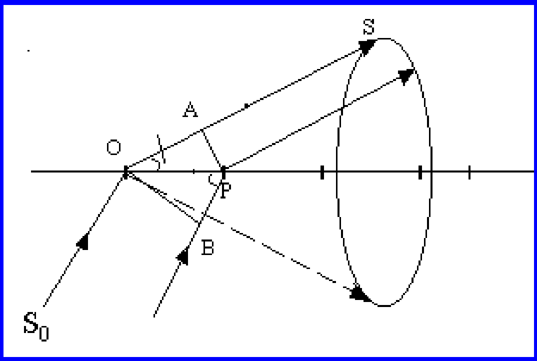
Where,

a— lattice parameter

α_0—angle which *a* makes with s_0

α— angle which *a* makes with *s*





Expanded to 3D lattice

$\boldsymbol{a}\cdot(\boldsymbol{s}-\boldsymbol{s}_0) = a(\cos\alpha-\cos\alpha_0) = h\lambda$

$\boldsymbol{b}\cdot(\boldsymbol{s}-\boldsymbol{s}_0) = b(\cos\beta-\cos\beta_0) = k\lambda$

$\boldsymbol{c}\cdot(\boldsymbol{s}-\boldsymbol{s}_0) = c(\cos\gamma-\cos\gamma_0) = l\lambda$

where,

a,b,c—lattice parameter

$\alpha_0,\beta_0,\gamma_0$—angle which *a* makes with s_0

α,β,γ —angle which *a* makes with *s*

h,k,l — indices of diffraction, integers

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 vector form (000) to (mnp):

T_{mnp} = ma + nb +pc

The differences in wavelengths:

$\Delta = T_{mnp} \cdot (s-s_0)$

$= (ma + nb + pc) \cdot (s-s_0)$

$= ma \cdot (s-s_0) + nb \cdot (s-s_0) + pc \cdot (s-s_0)$

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

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

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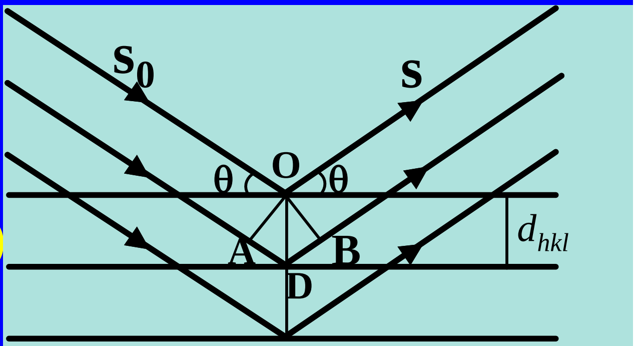
2. The Bragg's Law

Bragg discovered that you could consider the diffraction to have arisen from reflection from lattice planes



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

Condition for diffraction:

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

θ_n: the angle of reflection

n: the order of the reflection

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

Reformulated Laue equations:

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

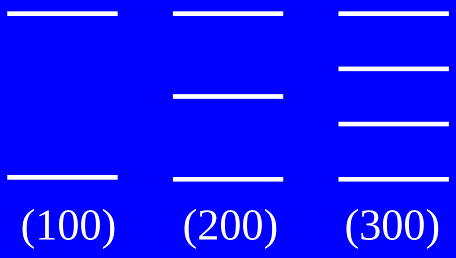
hkl — reflection indices

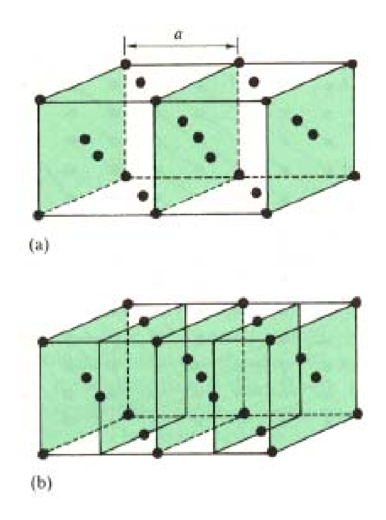
diffraction
crystal planes -

(100), (200), …

Families of planes

Lattice plane
directions-(100)





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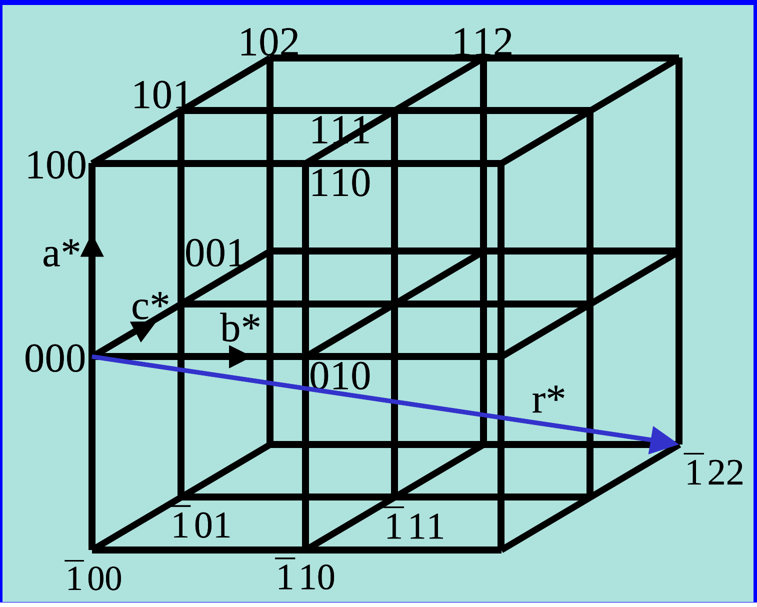
3. Reciprocal lattice

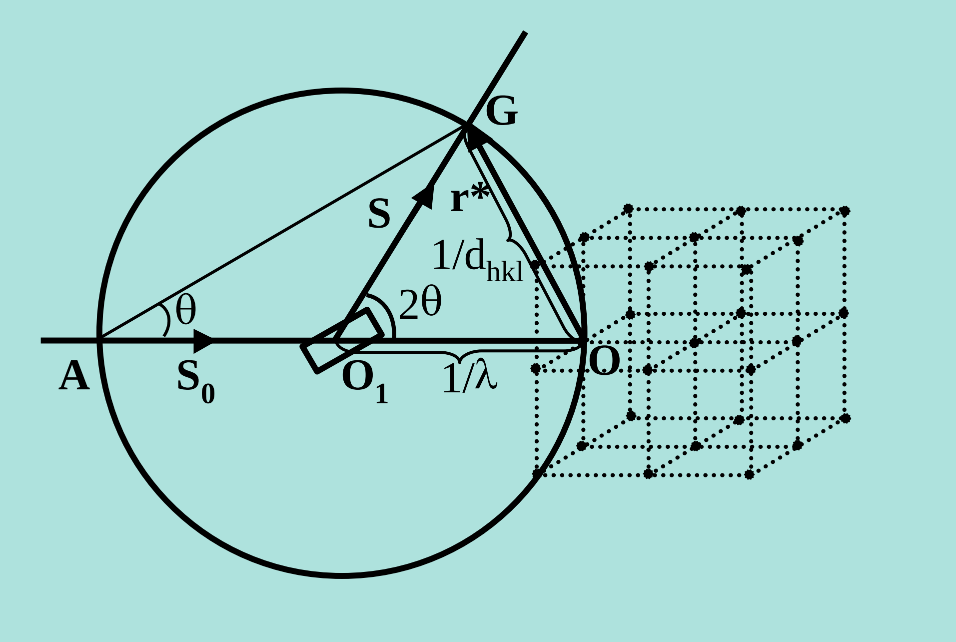
$$\vec{a}^* = \frac{\vec{b} \times \vec{c}}{V} \qquad \vec{b}^* = \frac{\vec{c} \times \vec{a}}{V} \qquad \vec{c}^* = \frac{\vec{a} \times \vec{b}}{V}$$

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

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

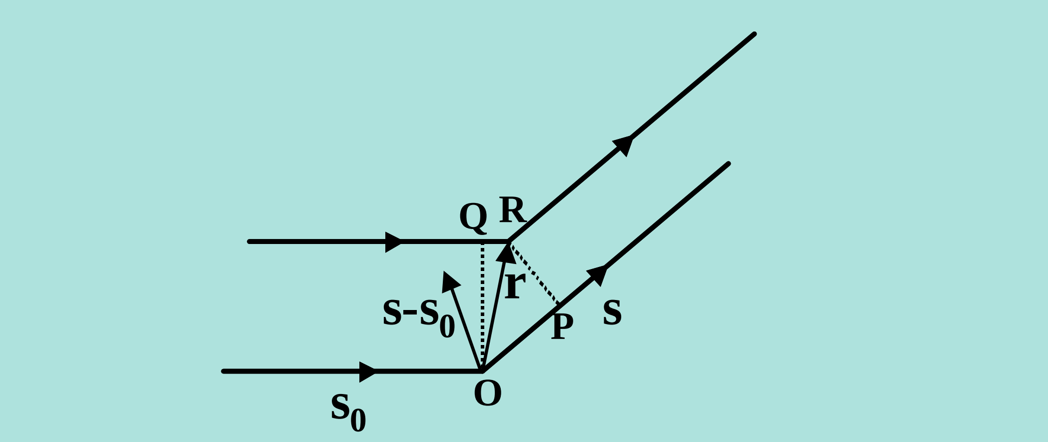


4. Ewald sphere



7.3.3. The intensity of diffraction beam

1. The principle of X-ray scattering

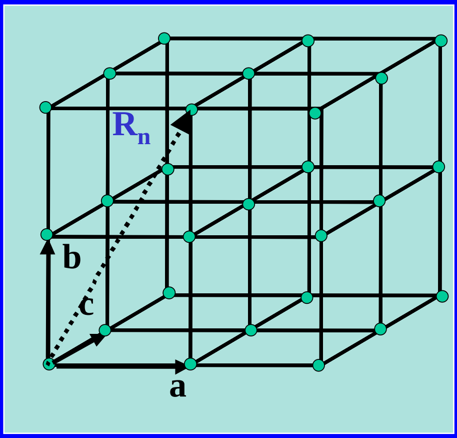


For elastic scattering, each electrons scatters the plane wave causing a spherical wave $(\exp 2\pi i(\boldsymbol{k}\cdot\boldsymbol{r}))$.

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

The scattered x-ray: $\exp 2\pi i[\mathbf{r}\cdot(\mathbf{s}-\mathbf{s}_0)/\lambda]$ or $\exp 2\pi i[\mathbf{r}\cdot\mathbf{q}/\lambda]$

The contribution of the scattering of all electrons:



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

For the crystal structure：

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

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

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

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

F(q) --- structure factor

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

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.*

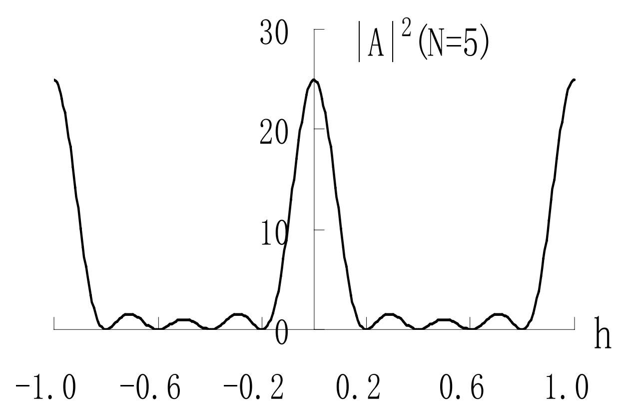
$$A_{mnp}=f\sum_{n_1=0}^{N_1-1}\sum_{n_2=0}^{N_2-1}\sum_{n_3=0}^{N_3-1}e^{2\pi i/\lambda(n_1\mathbf{a}+n_2\mathbf{b}+n_3\mathbf{c})\cdot\mathbf{q}}$$

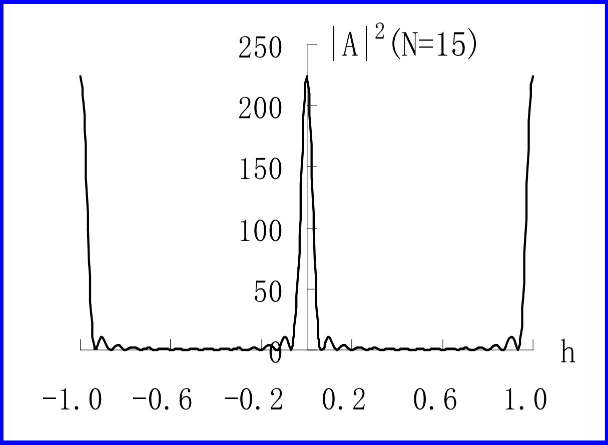
For the case of 1D and *f*=1,

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

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,

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

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

----- Laue conditions。

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

2. The intensity of diffraction beam

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

$$I_{hkl} = K|F_{hkl}|^2$$

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

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

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

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

The intensity of the diffraction beams are determined by the arrangement of atoms in the cell.

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3. systematic absence

Calculation for structure factor

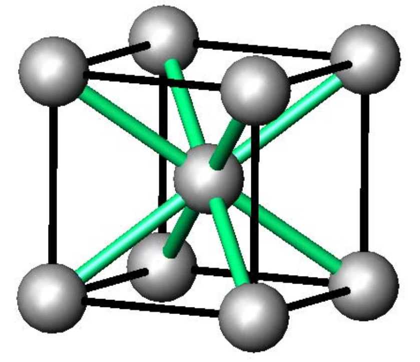
Example A, Body center crystal

$$F_{hkl} = \sum^{N/2} \{\exp(i\,2\pi(hx_j+ky_j+lz_j)) + \exp(i\,2\pi(h(x_j+1/2)+k(y_j+1/2)+l(z_j+1/2)))\}$$

$$= \sum_{j=1}^{N/2} \exp(i\,2\pi(hx_j+ky_j+lz_j))\,(1+\exp(i\pi(h+k+l)))$$

While $h+k+l = 2n+1$, $F_{hkl} = 0$;

systematic absence



Example II. Unit cell has a 2_1 screw axis along the c axis at x=y=0

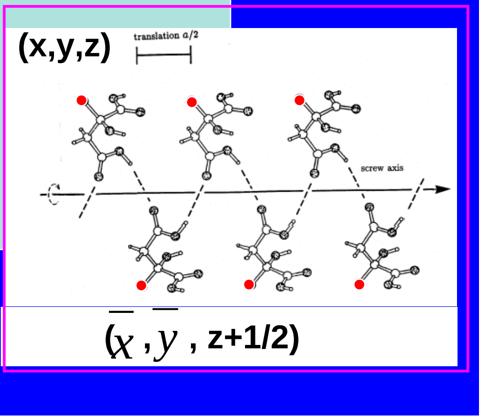
Equivalent position (x,y,z) and (-x , -y , z+1/2)

$$F_{hkl} = \sum_{j=1}^{N/2} f_j \exp[2\pi i(hx_j+ky_j+lz_j)] + \sum_{j=1}^{N/2} f_j \exp 2\pi i[(h\bar{x}+k\bar{y}+l(z_j+1/2)]$$

$$F_{00l} = \sum_{j=1}^{N/2} f_j \exp 2\pi i\,(lz_j)] + \sum_{j=1}^{N/2} f_j \exp 2\pi i\, l(z_j+1/2)$$

$$= \sum_{j=1}^{N/2} f_j \exp 2\pi l\,(lz_j)](1+\exp 2\pi i \cdot l/2)$$

$$= \begin{cases} 2\sum_{j=1}^{N/2} f_j \exp 2\pi i\,(lz_j)] & (l=2n) \\ 0 & (l=2n+1) \end{cases}$$



systematic absence

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systematic absence

Crystal structure which contain centering, glide plane and screw axis will have systematic absences.

Namely, some reflections will be systematically absent

systematic absence and sysmmetry

Types of reflection	Conditions for extinction	Cause of extinction	Centering and symmetry elements
hkl	$h+k+l$=odd	In-centred (bodycentred)	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)
okl	k =odd	Translation in b/2	b
	l =odd	(100) c/2	c
	$k+l$ =odd	glid (b+c)/2	n
	$k+l$ not multiples of 4	Planes (b+c)/4	d
00l	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	(oo1) c/4	$4_1, 4_3$
	l not multiples of 6	Screw axis c/6	$6_1, 6_5$

7.2.4 Applications of X-ray diffraction

1. Methods

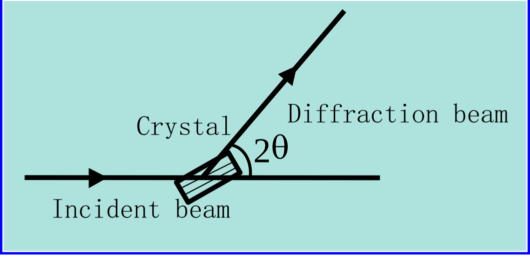
*** Single crystal diffraction**

Monochromatic camera method -- Monochromatic X-ray

Rotation, Oscillation, Weissenberg …

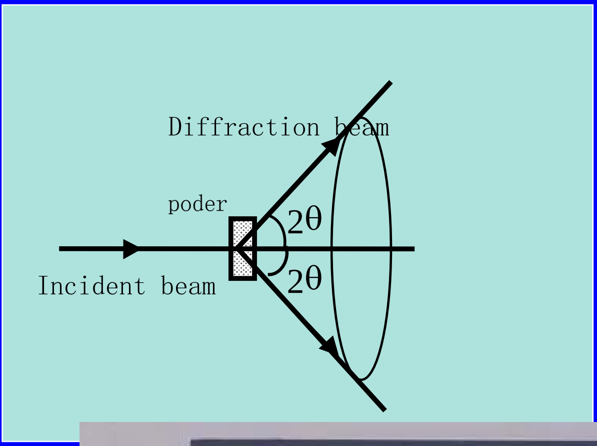
Laue photography --- white X-ray

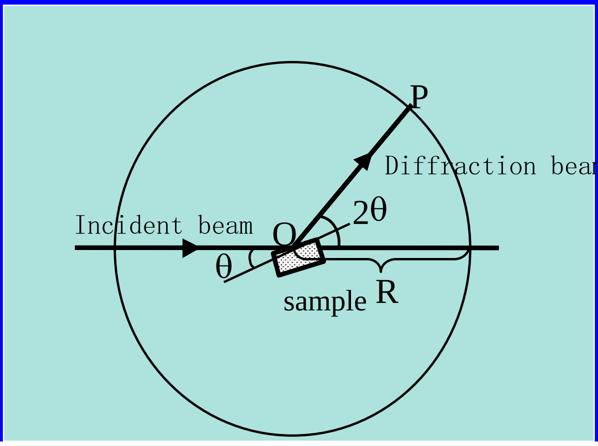
Diffractometer -- Monochromatic X-ray



* Powder diffraction

Monochromatic X-ray





Powder Diffractometer

Radiation sources

X-ray tubes

Synchrotron radiation

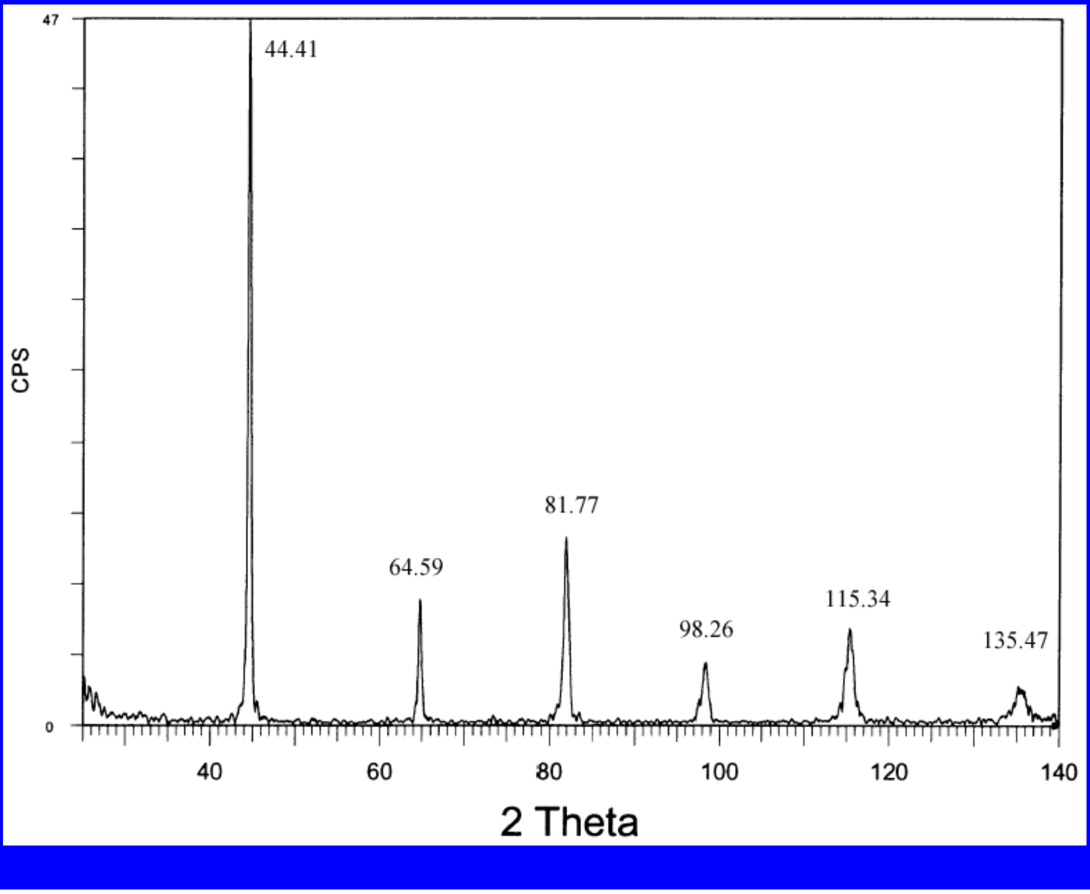
Monochromator – e.g.HOPG

Filter – e.g. Ni for CuKα

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

Automated diffractometer method



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2. The applications

a. crystal structure determination

Intensity data collection

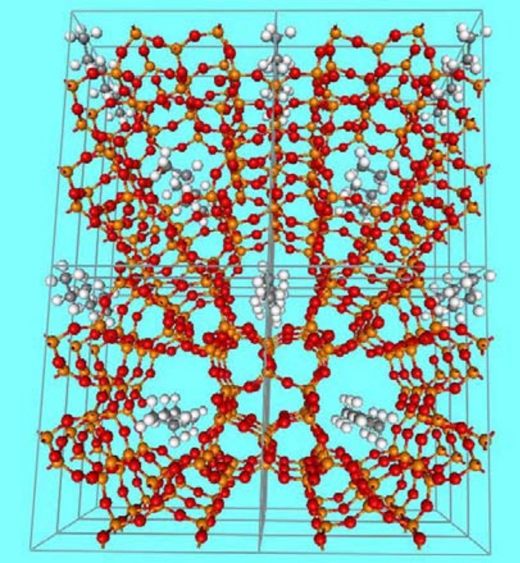
Indexing

Crystal system and Cell parameters

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

Phase problem

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



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

Indexing of the cubic system:

$$d_{hkl} = \frac{a_0}{\sqrt{h^2+k^2+l^2}}$$

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

$$\sin^2\theta \propto h^2+k^2+l^2 \rightarrow \sin^2\theta_1 : \sin^2\theta_2 : \sin^2\theta_{31} : \sin^2\theta_{41} :$$

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

Characteristic line sequence in cubic system:

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, …

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,* 222, *300,* ….

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

Example for the indexing of cubic system and its applications

Sample: NaCl

Condition: Cu Kα, λ=1.5418Å, R=50mm

(1) Measure sample and relative intensity

(2) Calculate the position of diffraction lines (usually 2θ)

(3) Calculate θ in according to the formulae

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

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

(6) Identify Bravais lattice → face cubic

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

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

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

---

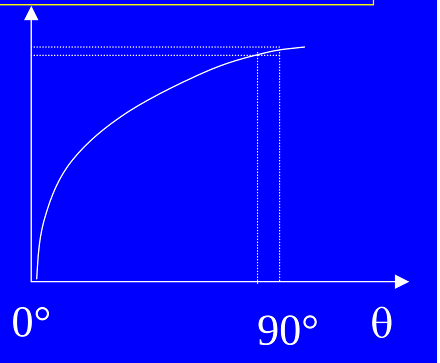
(8) Calculate lattice parameter

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

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

a=5.628 Å

Why use high angle values?



(9) ρ= 2.165g/cm³ for NaCl

$$n = \frac{\rho V}{\frac{M}{N_0}} = \frac{2.165\times(5.628\times10^{-8})}{\frac{23+35.5}{6.022\times10^{23}}} = 4$$

One unit cell contains 4 NaCl

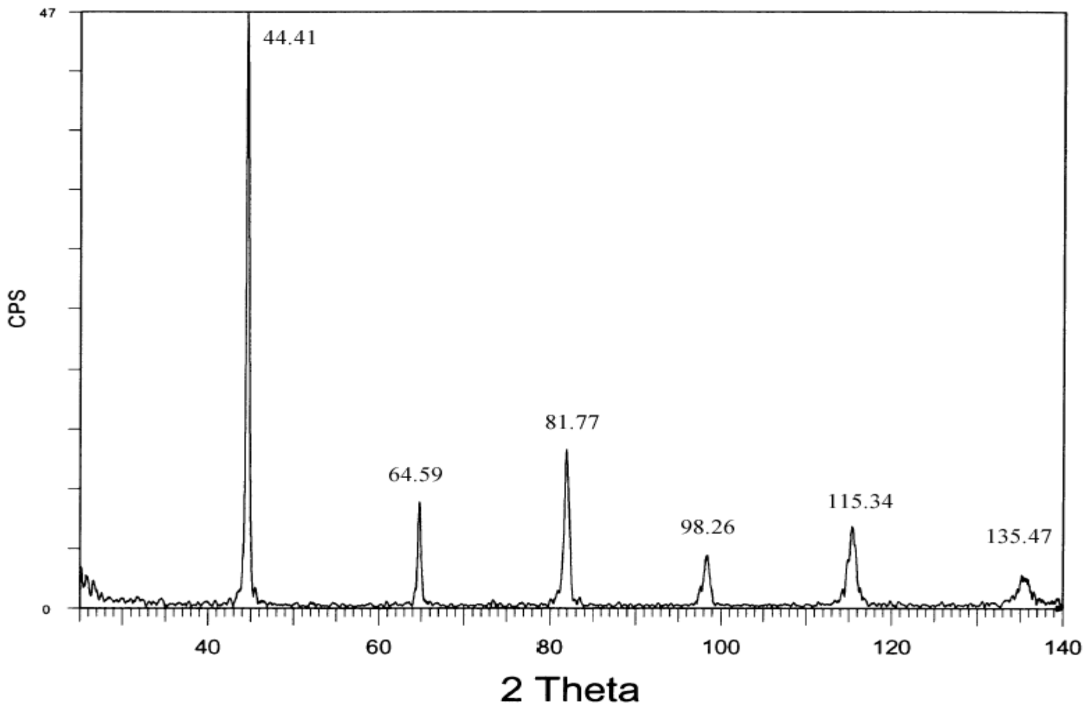
Example. Index cubic pattern and calculation lattice parameter

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	28.26	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

If λ=1.5418 Å,

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

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

---

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

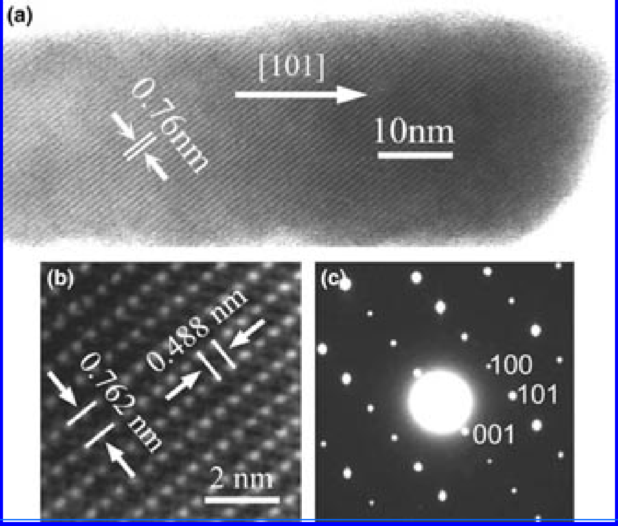
Radical distribution function (for amorphous materials)

7.2.5 Electron Diffraction and Neutron Diffraction

1. Electron Diffraction

$$\lambda = \frac{h}{\sqrt{2meV}}$$

100 kV ---- 0.00370 nm



a) TEM image of the tip part of one TeO2 nanorod. (b)Enlarged TEM image. (c) The corresponding electron diffraction pattern.

2. Neutron Diffraction

----- Scatterring of atomic nuclear

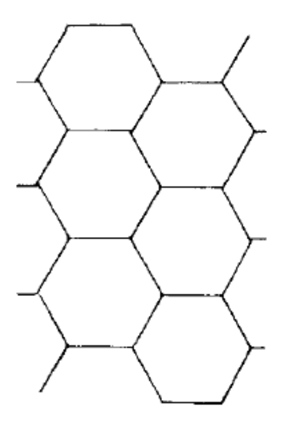
7.3 Quasi-crystal, liquid crystal and amorphous

Quasi-crystal

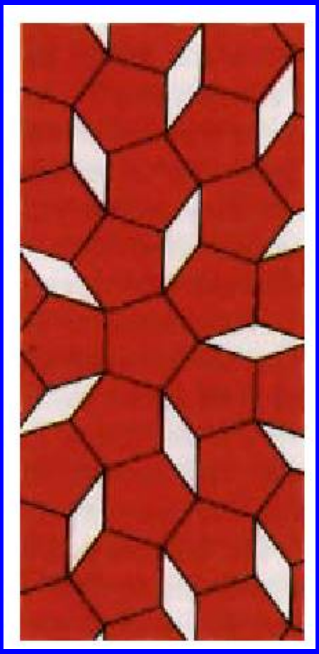
Liquid crystal

Amorphous

Crystal



Quasi-crystal



There is no translation symmetry.