Analisis Difraksi Sinar-X
(X-Ray Diffraction Analysis)

Crystal Structure

Ideal Crystal: Mengandung susunan atom/ion secara periodik
Direpresentasikan oleh titik kisi
Sekelompok atoms yang membentuk titik kisi

Basis

LATTICE = Kisi susunan titik dalam ruang yang memiliki lingkungan identik antara satu dengan lainnya

CRYSTAL STRUCTURE = Susunan atom (kelompok atom) yang berulang .

It can be described by associating with each lattice point a group of atoms called the **MOTIF** (**BASIS**)
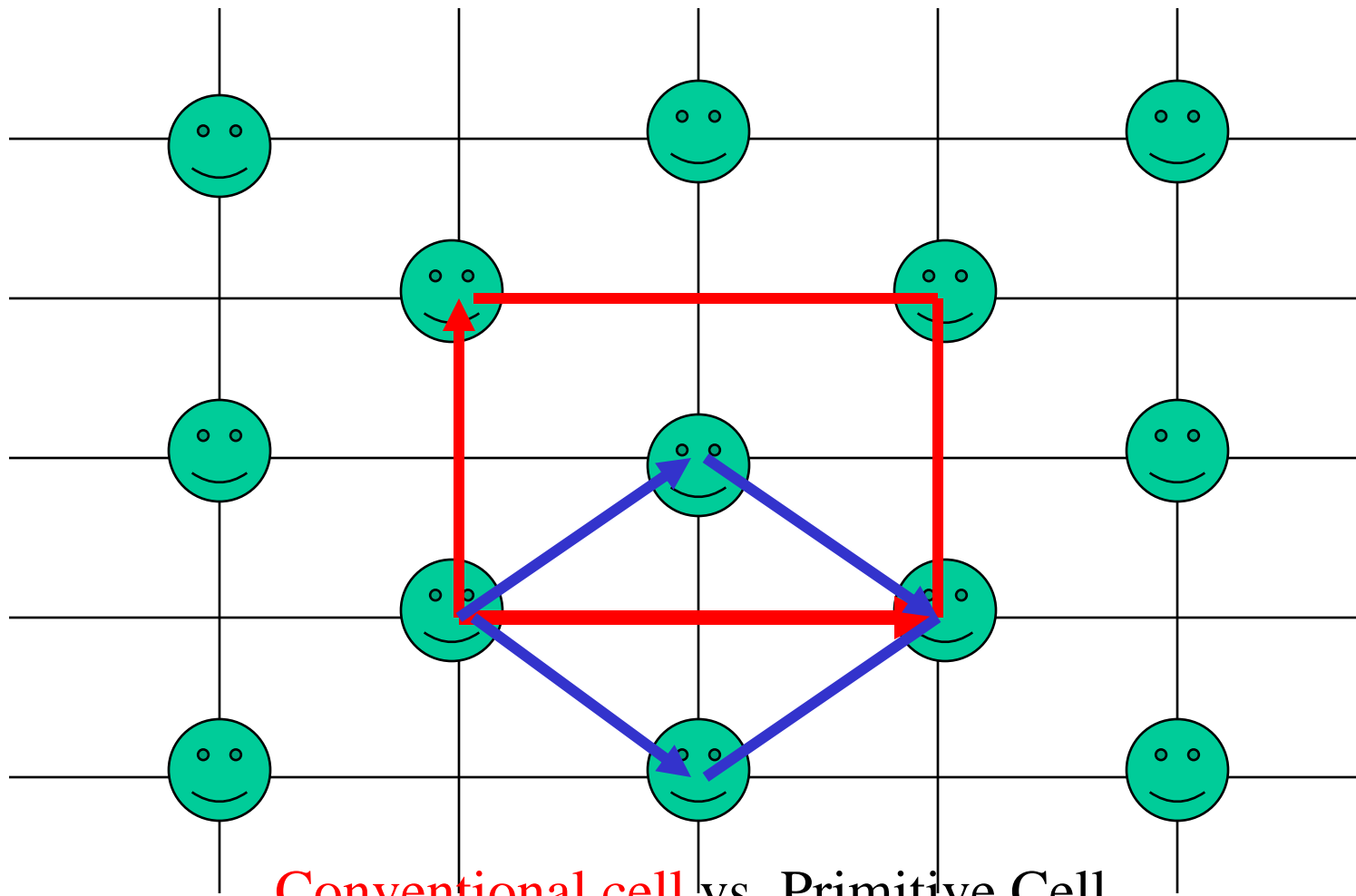
LATTICE

Translational vector

BASIS / MOTIF

CRYSTAL STRUCTURE
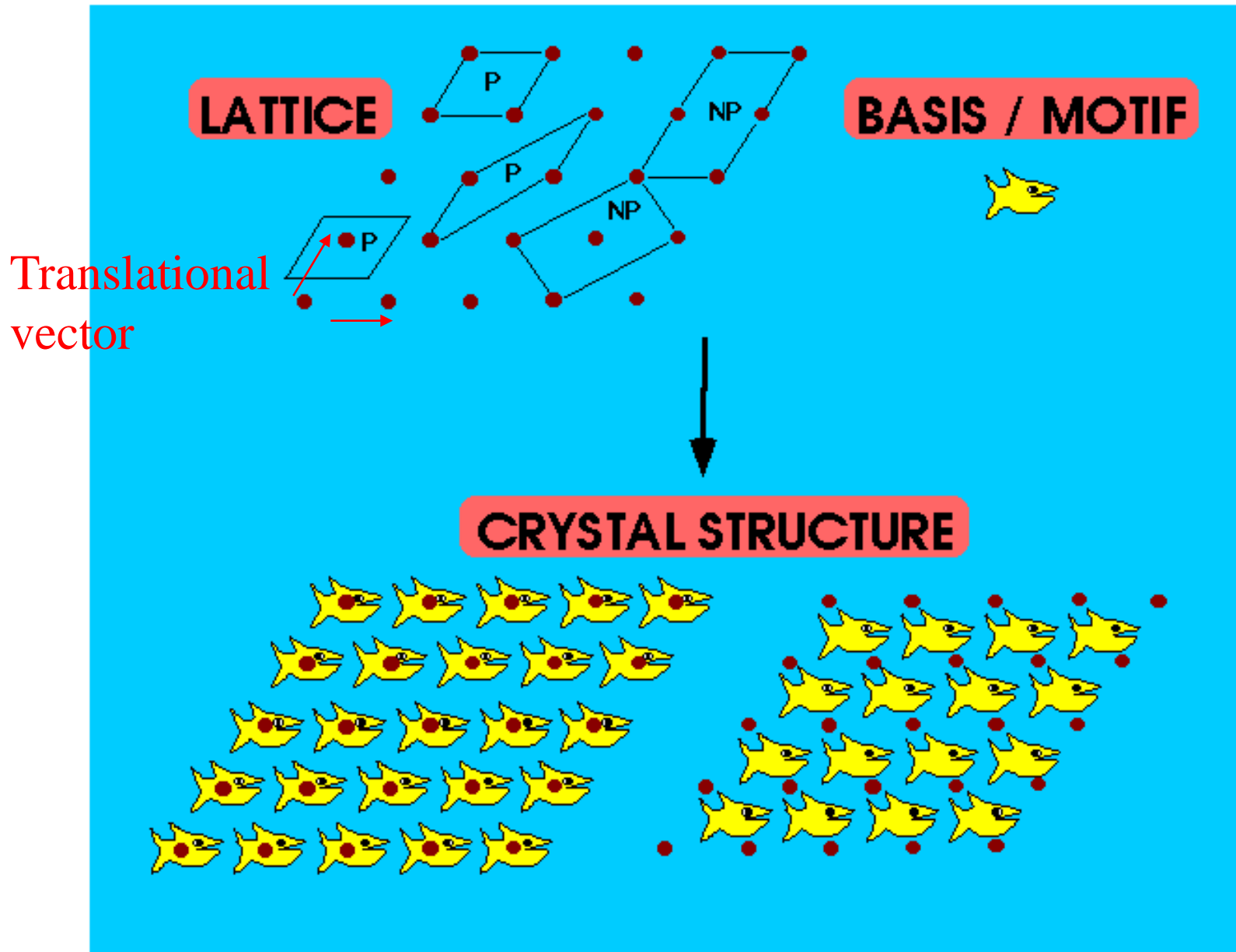
$$\{R = n_1 \, \mathbf{a}_1 + n_2 \, \mathbf{a}_2 + n_3 \, \mathbf{a}_3\}$$
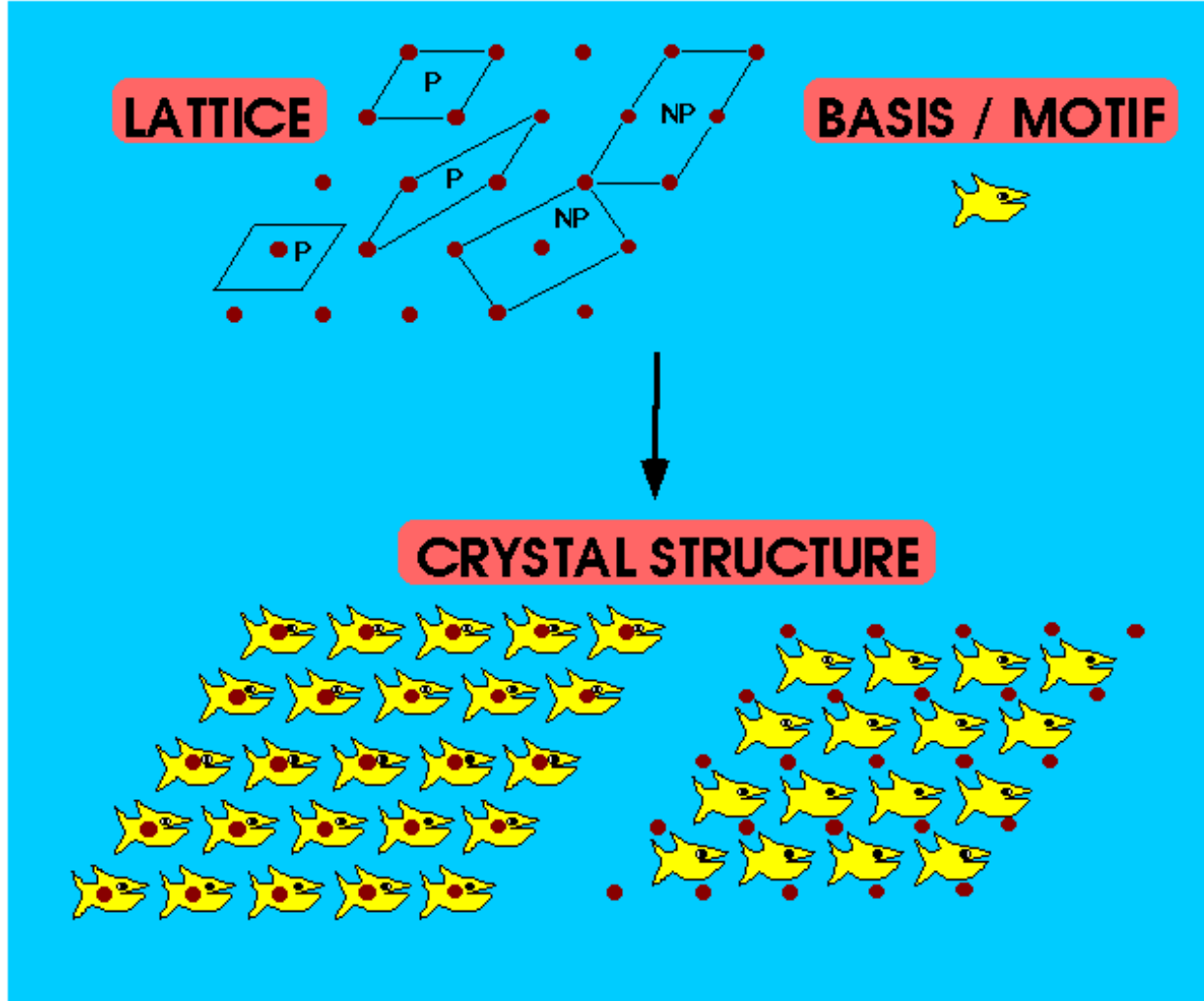
UNIT CELL = *The smallest component of the crystal, which when stacked together with pure translational repetition reproduces the whole crystal*
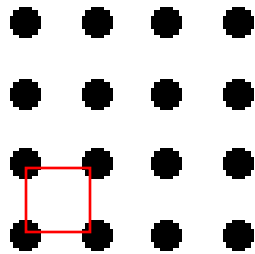**Primitive Cell**: *simplest cell, contain one lattice point*
                    Not necessary have the crystal symmetry
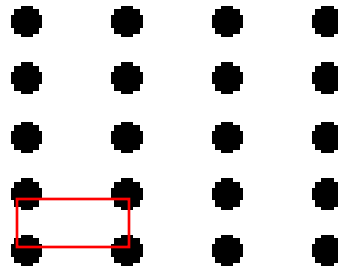
Conventional cell vs. Primitive Cell
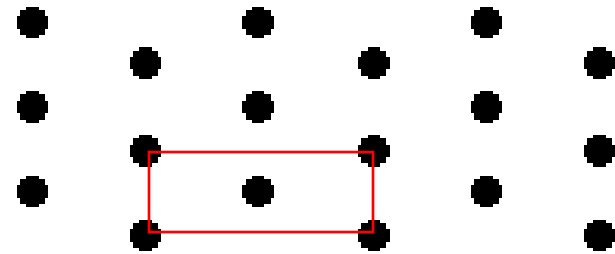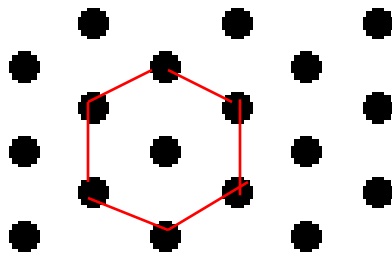*Reflecting the symmetry*
Different Basis

Square
P

Rectangular
P
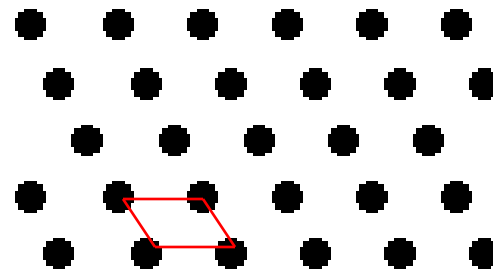
Centered Rectangular
NP

Hexagonal

Oblique

5 Kisi Bravais dalam 2D

Square	a=b	$\gamma = 90$
Rectangular	a≠ b	$\gamma = 90$
Centered Rectangular	a ≠b	$\gamma = 90$
Hexagonal	a=b	$\gamma = 120$
Oblique	a ≠b	$\gamma \neq 90$

5 Kisi Bravais dalam 2D

2D LATTICE

Translational vector
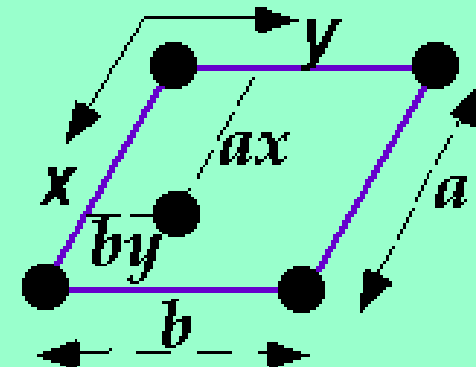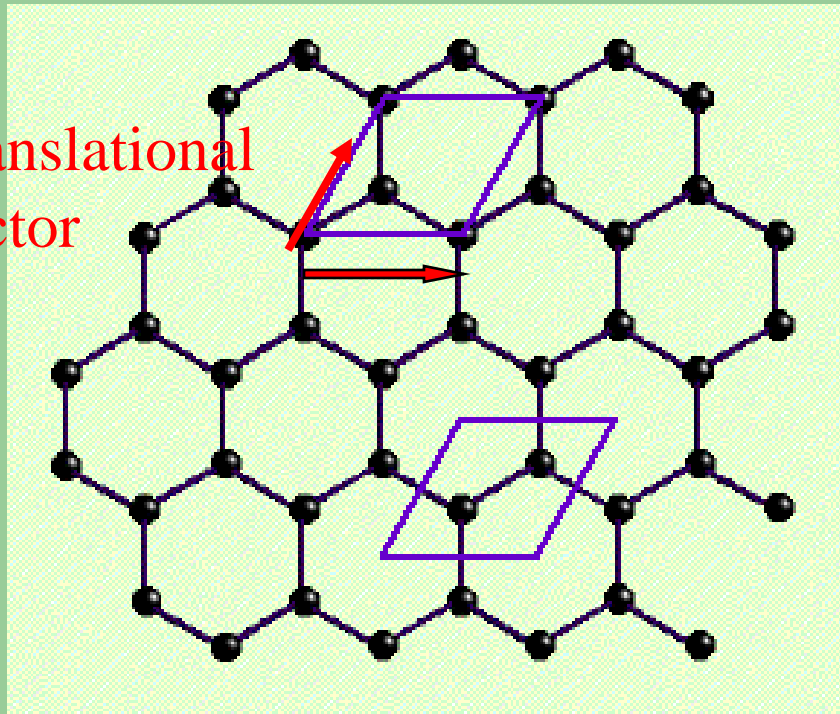
Atom 1: (0, 0)
Atom 2: ($2/3$, $1/3$)

Unit Cells
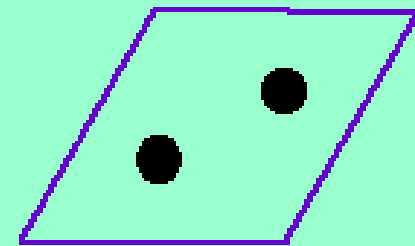
Atom 1: ($2/3$, $1/3$)
Atom 2: ($1/3$, $2/3$)

FRACTIONAL Atomic (x,y) coordinates
(As a fraction of unit cell dimension)
i.e. true dimensions are ax and by

Definition:

3D: 14 Bravais Lattice, 7 Crystal System

Bravais Lattice: an infinite array of discrete points with an arrangement and orientation that appears exactly the same from whichever of the points the array is viewed.

| Name	Number of Bravais lattices	Conditions
Triclinic	1 (P)	$a_1 \neq a_2 \neq a_3$ $\alpha \neq \beta \neq \gamma$
Monoclinic	2 (P, C)	$a_1 \neq a_2 \neq a_3$ $\alpha = \beta = 90 \neq \gamma$
Orthorhombic	4 (P, F, I, A)	$a_1 \neq a_2 \neq a_3$ $\alpha = \beta = \gamma = 90$
Tetragonal	2 (P, I)	$a_1 = a_2 \neq a_3$ $\alpha = \beta = \gamma = 90$
Cubic	3 (P, F, I)	$a_1 = a_2 = a_3$ $\alpha = \beta = \gamma = 90$
Trigonal	1 (P)	$a_1 = a_2 = a_3$ $\alpha = \beta = \gamma < 120 \neq 90$
Hexagonal	1 (P)	$a_1 = a_2 \neq a_3$ $\alpha = \beta = 90$ $\gamma = 120$

Kisi FCC
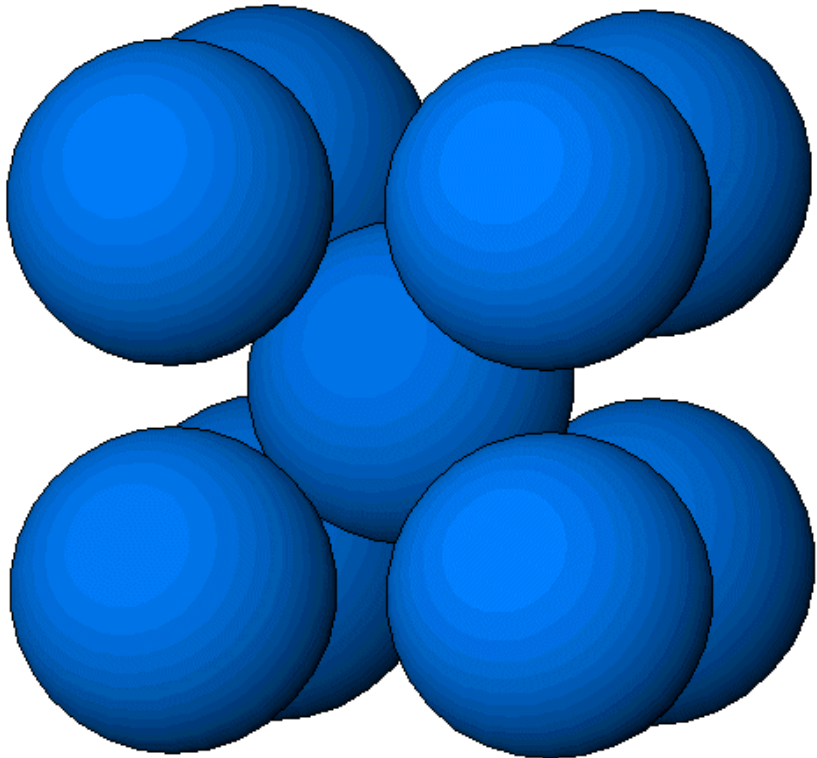
Logam Cu memiliki kisi **face-centered cubic**

Atom-atom identik terletak pada sudut dan pada bagian muka kisi

Jenis Kisi adalah type F

also Ag, Au, Al, Ni...
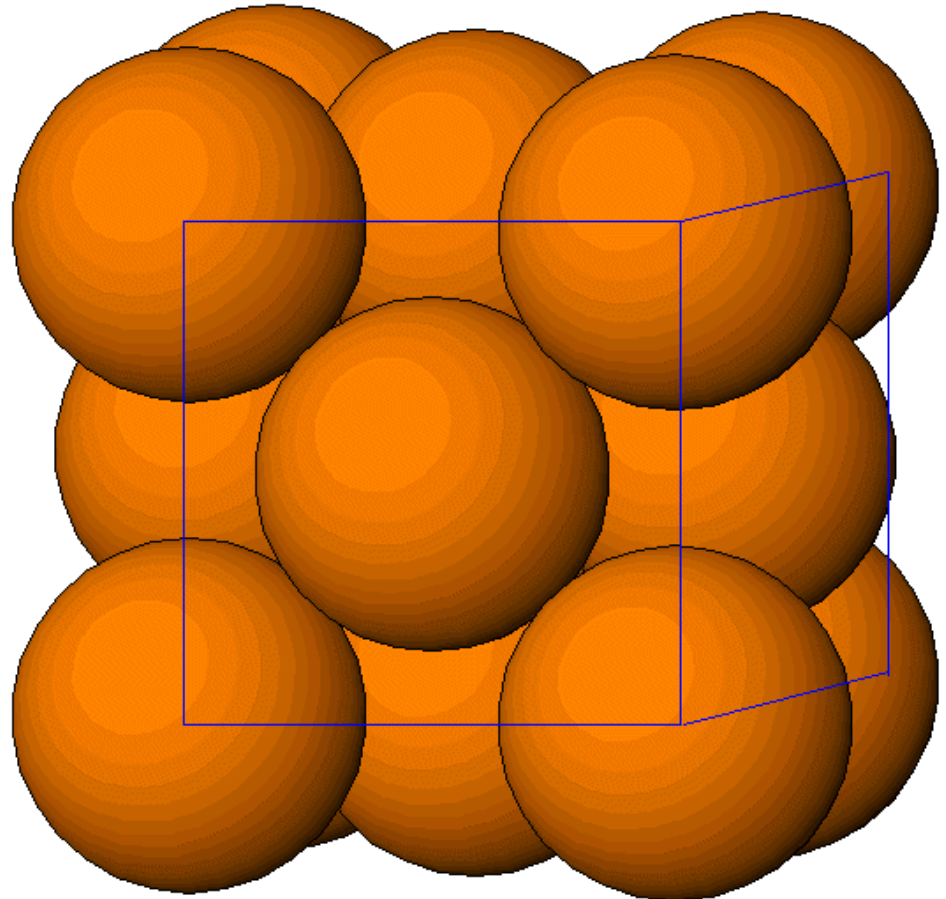
BCC Lattice

α-Fe merupakan sebuah kisi **body-centered cubic**

Atom-atom Identik terletak pada sudut dan body center (nothing at face centers)
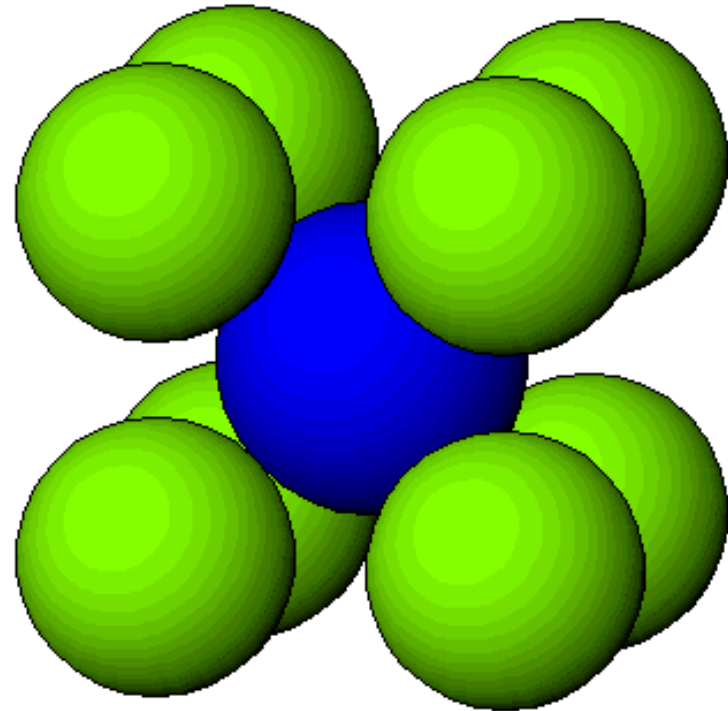
Lattice type I

Also Nb, Ta, Ba, Mo...

Simple Cubic Lattice

Caesium Chloride (CsCl) is **primitive cubic**

Different atoms at corners and body center. NOT body centered, therefore.

Lattice type P

Also CuZn, CsBr, LiAg

BUCKMINSTERFULLERENE
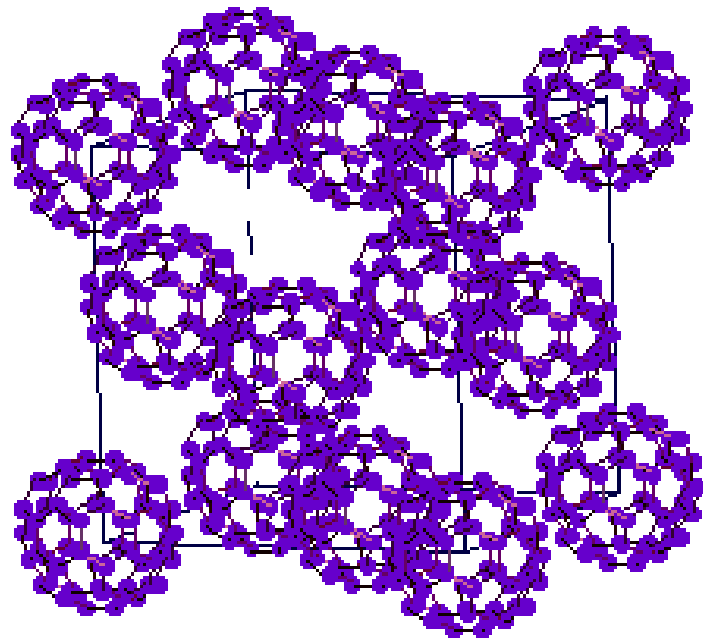
FCC

FOOT & MOUTH VIRUS

BCC

FCC Lattices
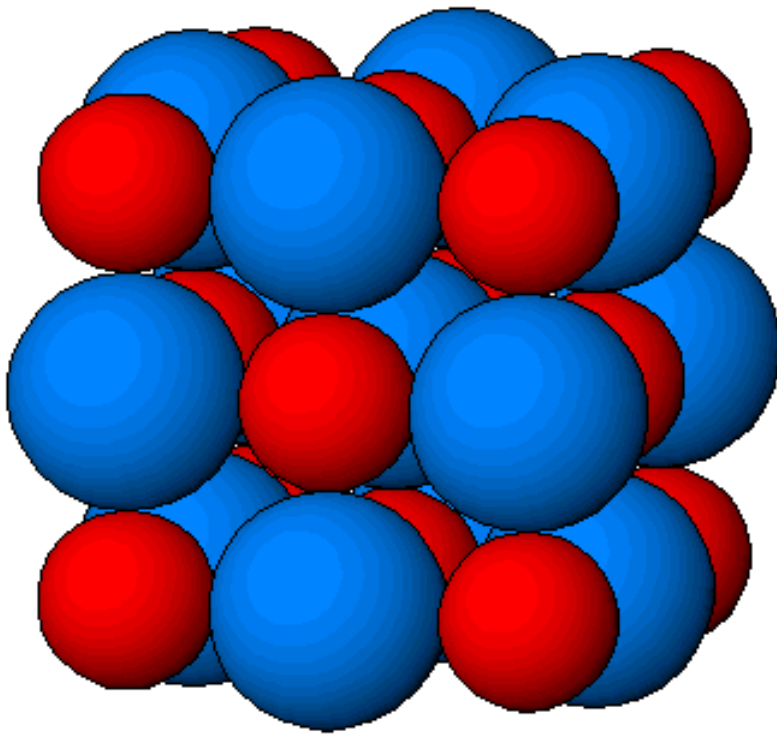
Sodium Chloride (NaCl) - Na is much smaller than Cs

Face Centered Cubic

Rocksalt structure

Lattice type F

Also NaF, KBr, MgO….

Diamond Structure: two sets of FCC Lattices
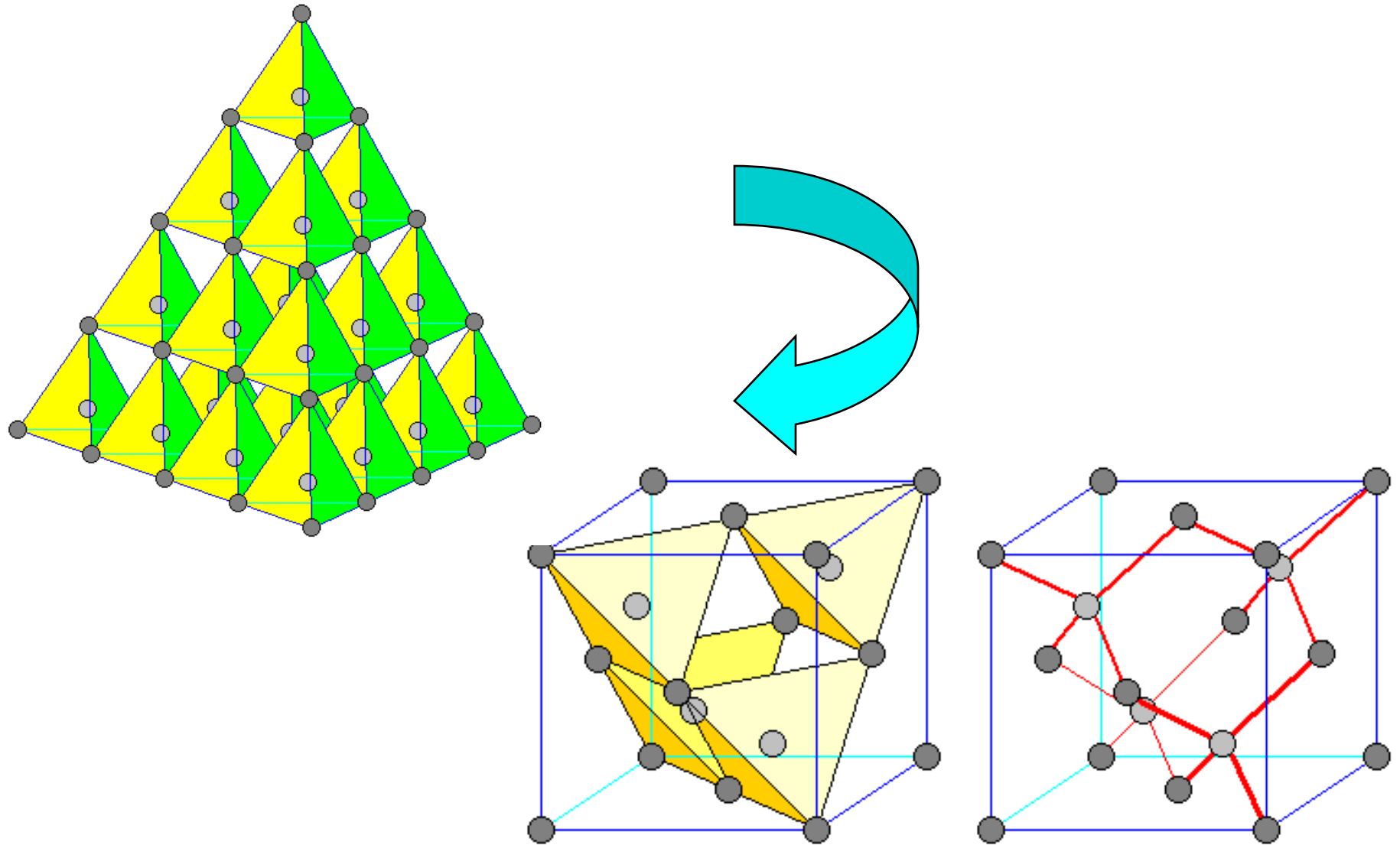
Tetragonal: P, I

One 4-fold axes
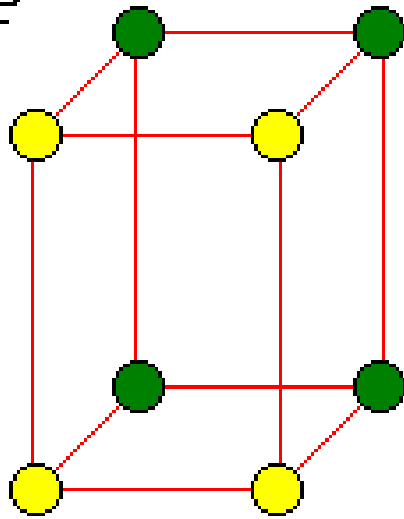
P   I
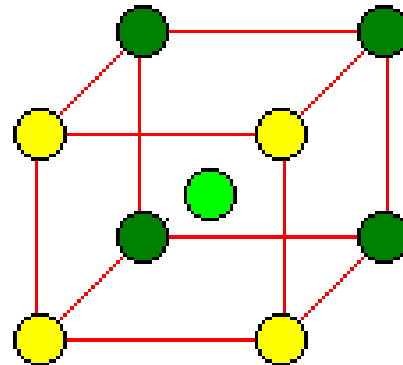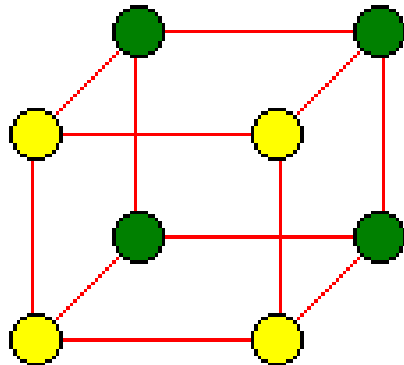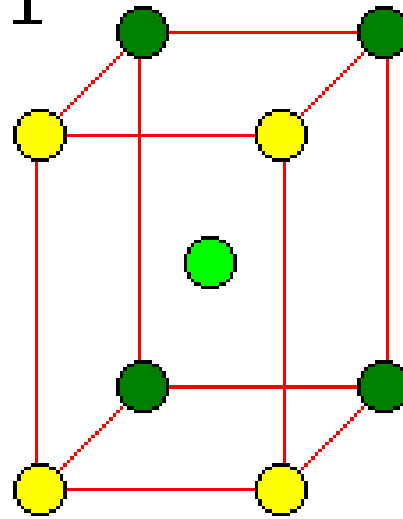
Why not F tetragonal?

Example

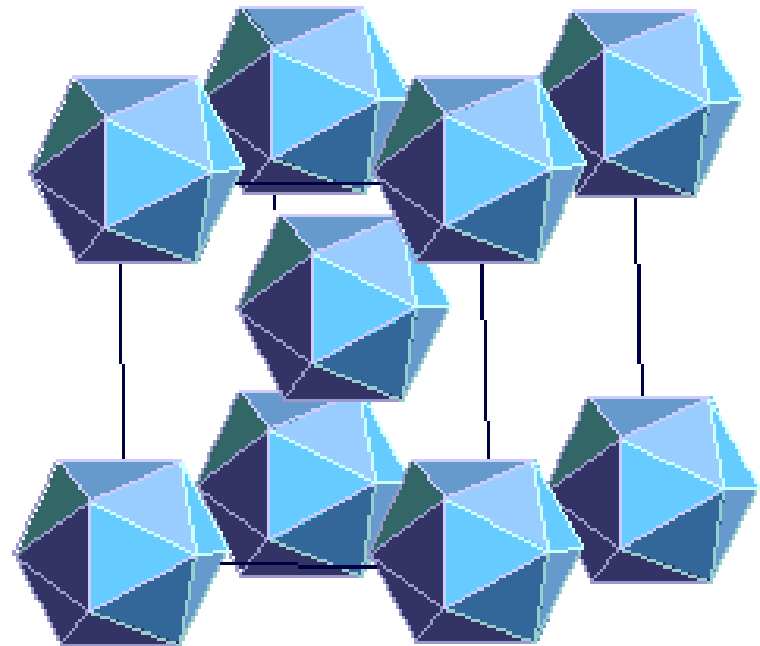CaC$_2$ - has a rocksalt-like structure but with non-spherical carbides

$$\begin{bmatrix} \mathbf{C} \\ \| \| \| \\ \mathbf{C} \end{bmatrix}^{2-}$$
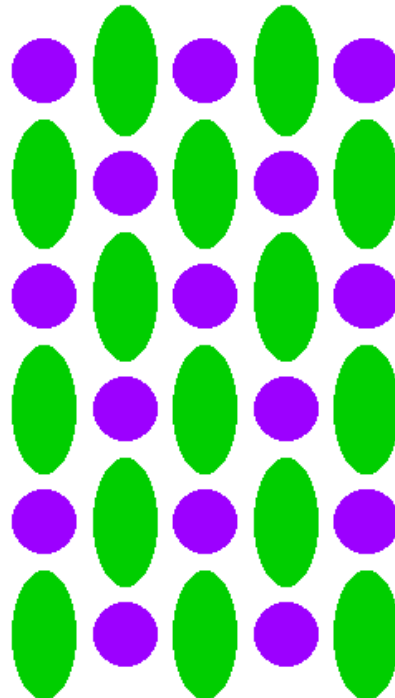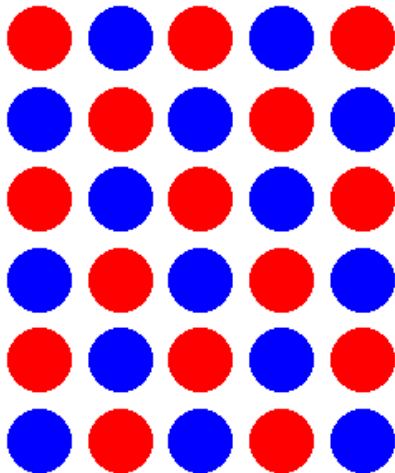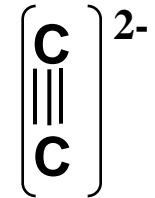
Carbide ions are aligned parallel to **c**

$\therefore$ **c > a,b** $\rightarrow$ tetragonal symmetry

Orthorhombic: P, I, F, C
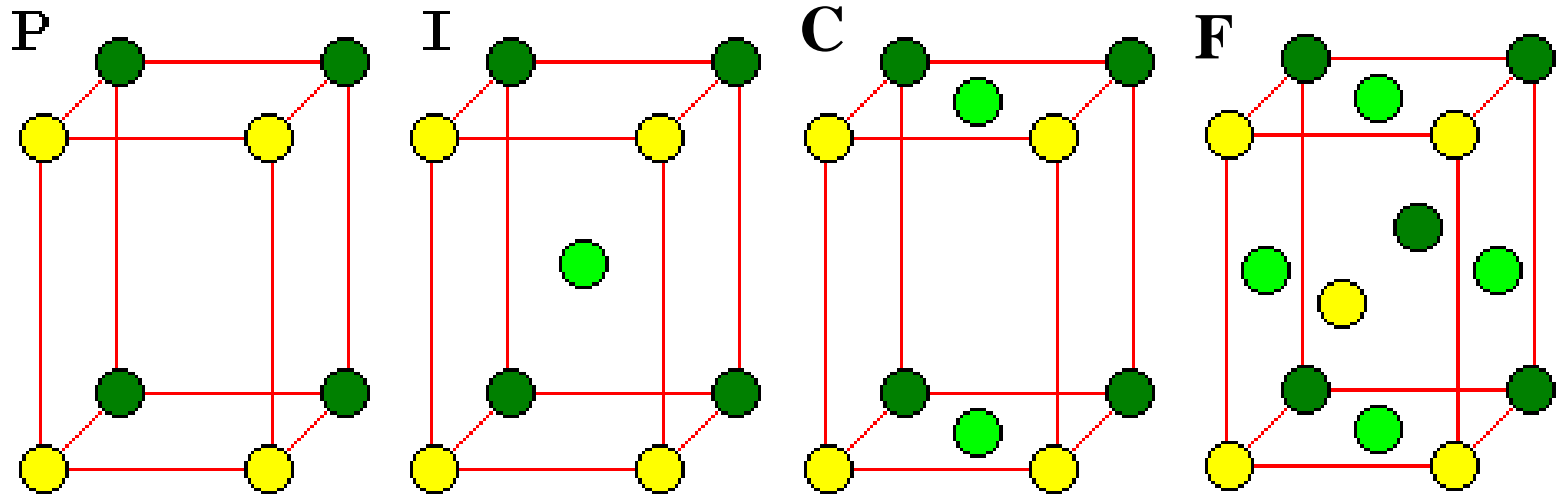
Another type of centering

Side centered unit cell

Notation:

A-centered if atom in bc plane

B-centered if atom in ac plane

C-centered if atom in ab plane
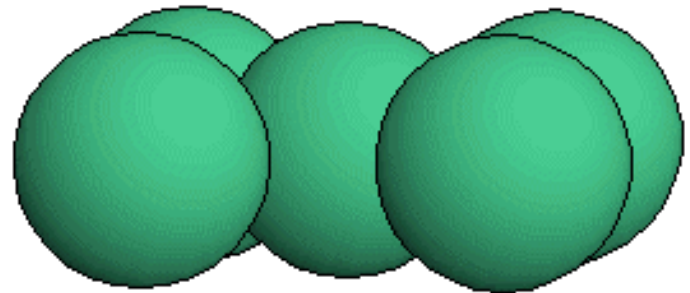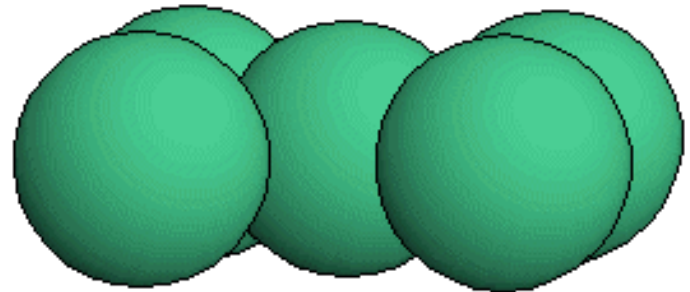
Unit cell contents

Counting the number of atoms <u>within</u> the unit cell
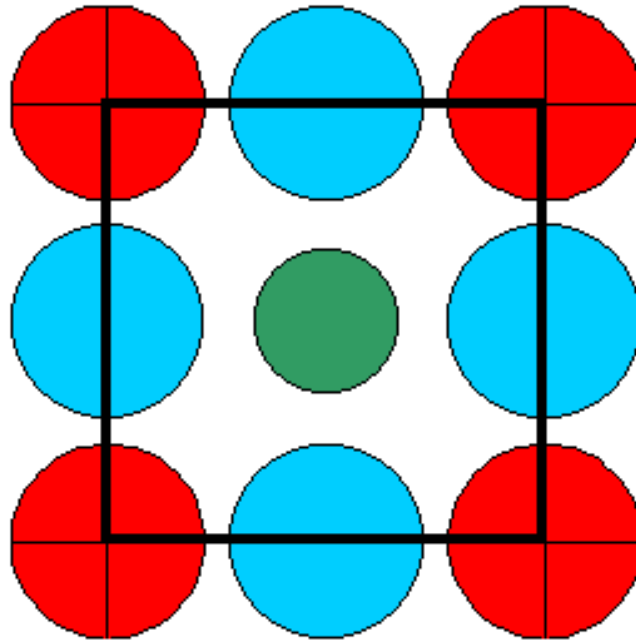
Many atoms are <u>shared</u> between unit cells

Atoms	**Shared Between:**	**Each atom counts:**
corner	8 cells	1/8
face center	2 cells	1/2
body center	1 cell	1
edge center	4 cells	1/4

lattice type	**cell contents**	
P	1	[=8 x 1/8]
I	2	[=(8 x 1/8) + (1 x 1)]
F	4	[=(8 x 1/8) + (6 x 1/2)]
C	2	[=(8 x 1/8) + (2 x 1/2)]
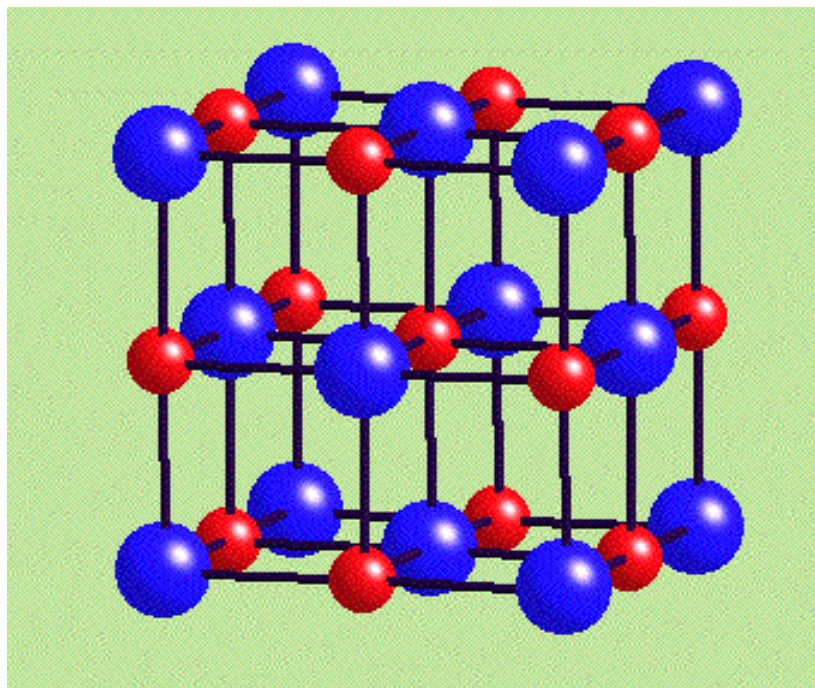
e.g. NaCl

Na at corners: $(8 \times 1/8) = 1$ Na at face centres $(6 \times 1/2) = 3$

Cl at edge centres $(12 \times 1/4) = 3$ Cl at body centre $= 1$

Unit cell contents are $4(Na^+Cl^-)$

Fractional Coordinates

(0,0,0)

(0, ½, ½)

(½, ½, 0)

(½, 0, ½)
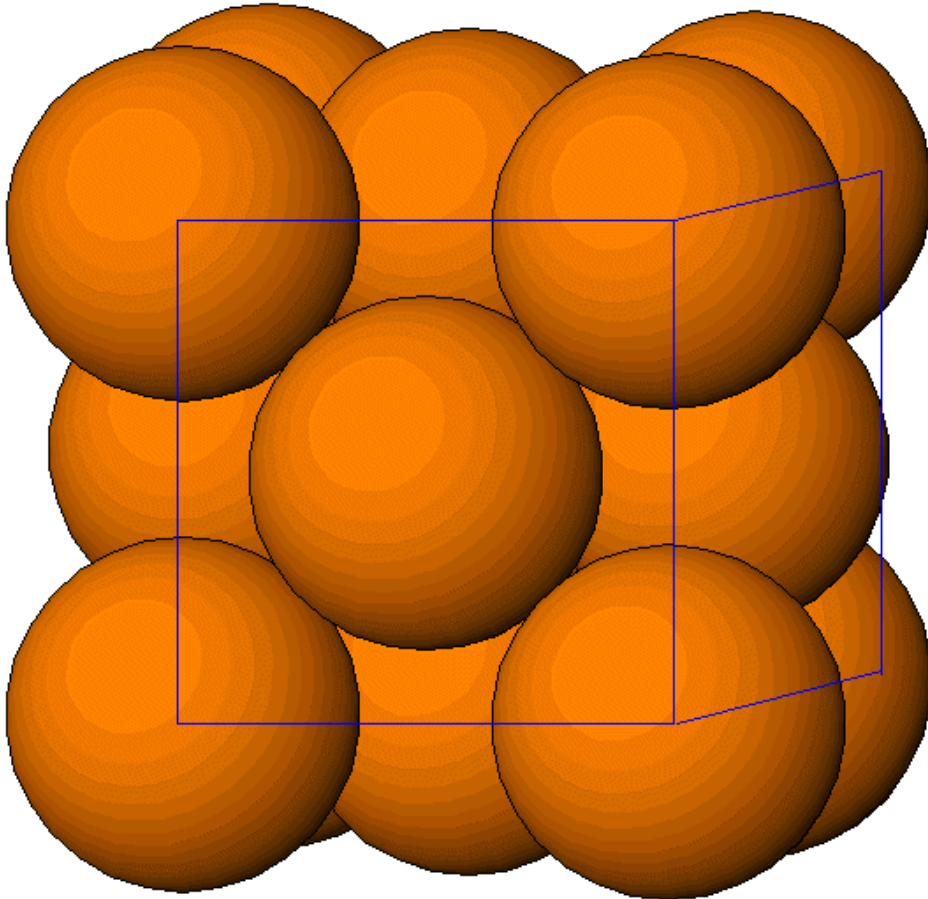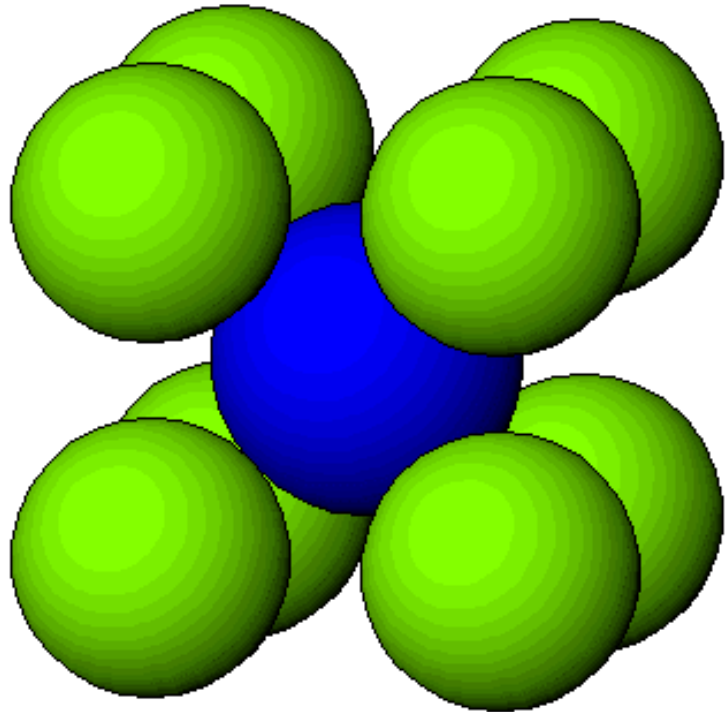
Cs (0,0,0)
Cl (½, ½, ½)

Density Calculation

$$\rho = \frac{nA}{V_C N_A}$$

n: number of atoms/unit cell

A: atomic mass

V_C: volume of the unit cell

N_A: Avogadro's number
   (6.023x10²³ atoms/mole)

Calculate the density of copper.

R_{Cu} =0.128nm, Crystal structure: FCC, A_{Cu}= 63.5 g/mole

$$n = 4\ atoms/cell, \qquad V_C = a^3 = (2R\sqrt{2})^3 = 16\sqrt{2}R^3$$

$$\rho = \frac{(4)(63.5)}{[16\sqrt{2}(1.28\times10^8)^3 \times 6.023 \times 10^{23}]} = 8.89\,g\,/\,cm^3$$

8.94 g/cm³ in the literature

Crystallographic Directions And Planes
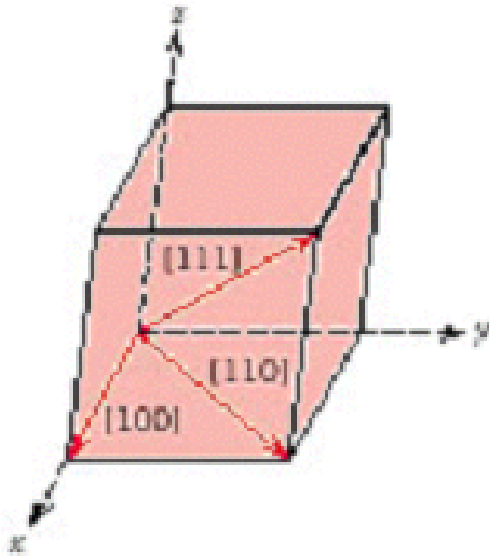
Lattice Directions

Individual directions: **[uvw]**

Symmetry-related directions: **<uvw>**

Miller Indices:

      1. Find the intercepts on the axes in terms of the lattice
          constant a, b, c

      2. Take the reciprocals of these numbers, reduce to the
          three integers having the same ratio

          (hkl)

Set of symmetry-related planes: {hkl}

Crystal Structures [OGN 21.2]

- Body-centered cubic

FIGURE 21.12 The b.c.c. structure. An atom is located at the center of each cubic cell (green) as well as at each corner of the cube (orange). The atoms are reduced slightly in size to make positions clear.

1/8 atom at 8 corners

1 at center
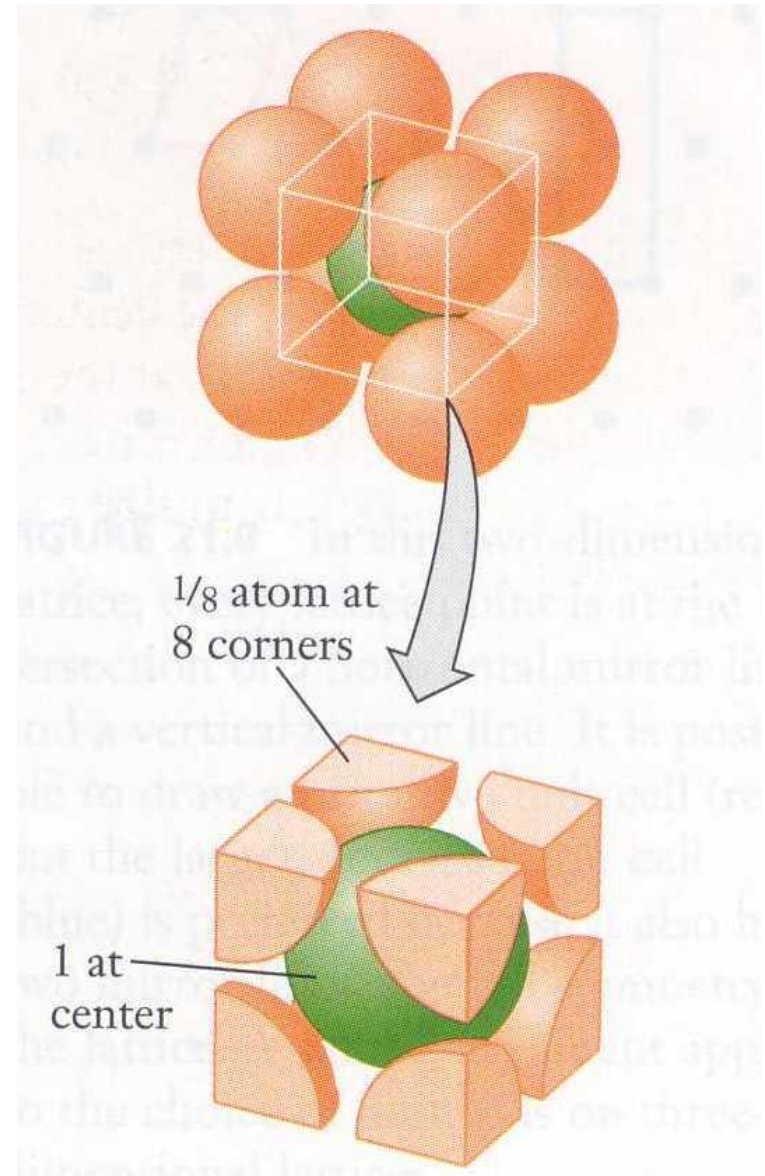
Lattice planes

◆ 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
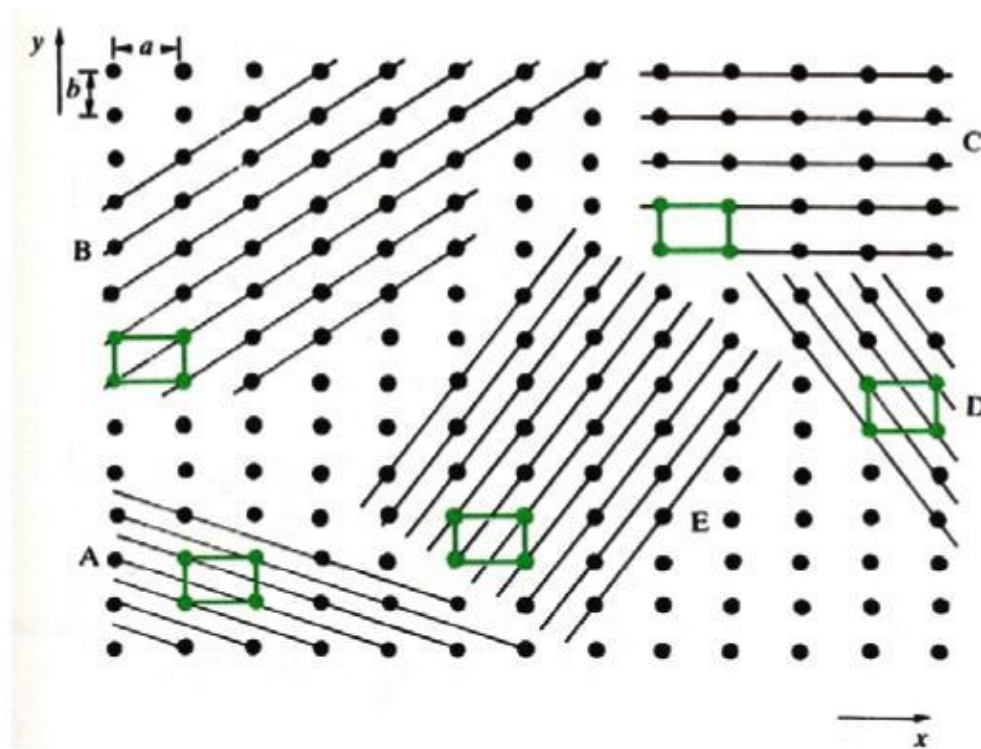
Examples of Miller indices

(100)   **(111)**
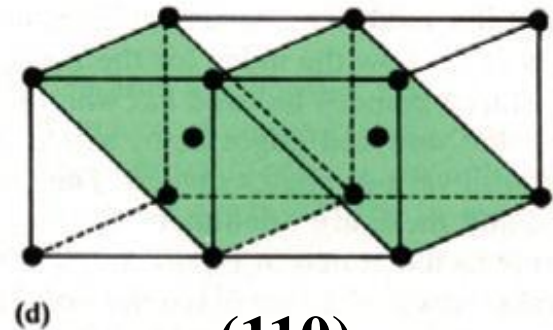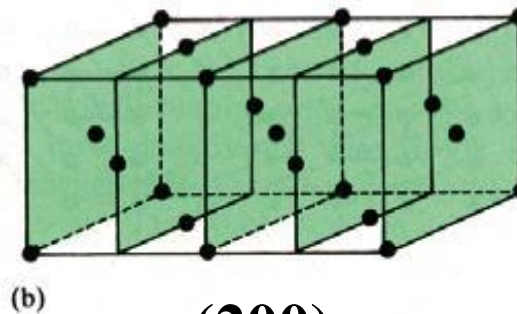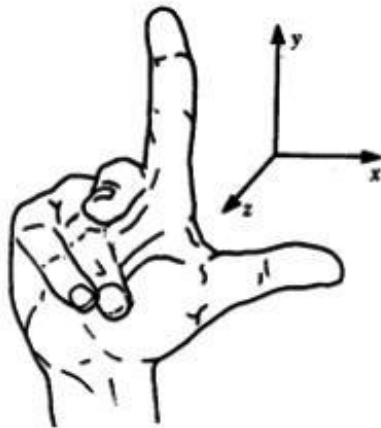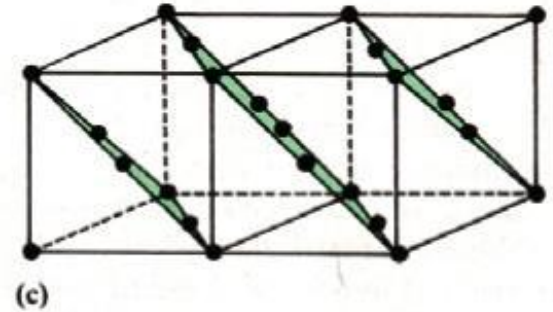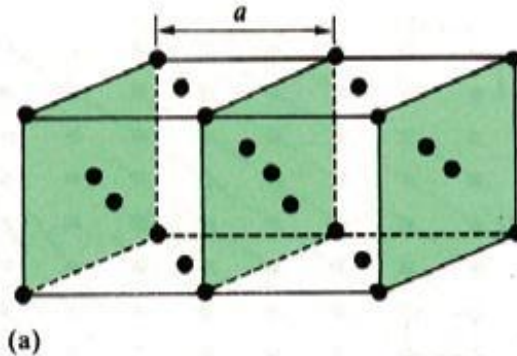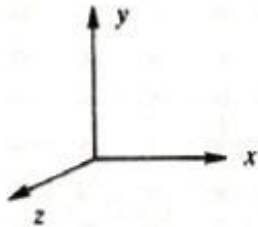
(200)   **(110)**

Families of planes

◆ Miller indices describe the orientation a spacing of a family of planes
  – The spacing between adjacent planes in a family is referred to as a "d-spacing"

Three different families of planes

d-spacing between (300) planes is one third of the (100) spacing

(100) (200) (300)
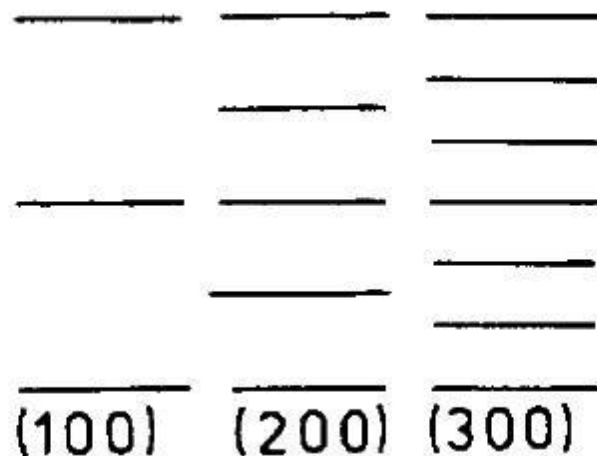
Lattice spacing

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

For cubic system

(a)

(c)
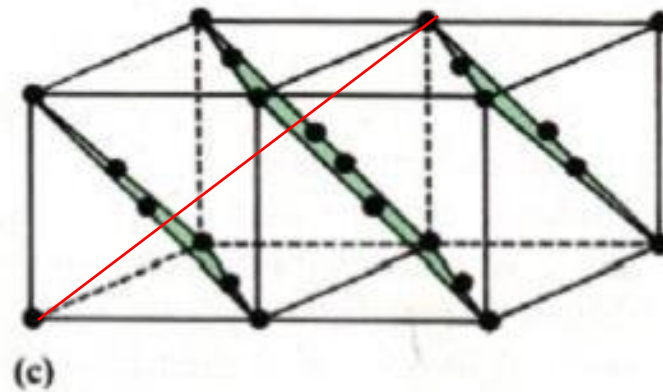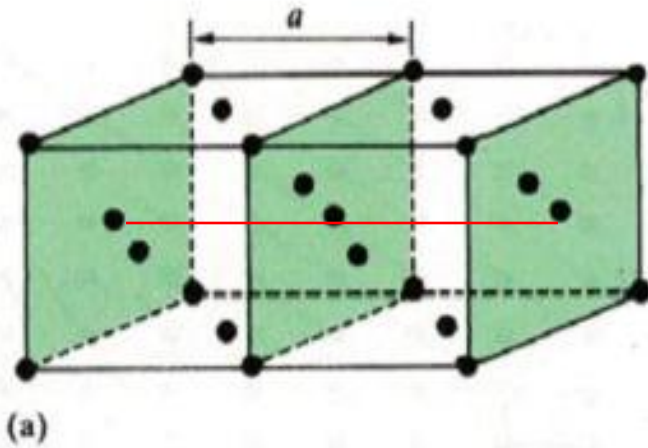
d-spacing formulae

- For a unit cell with orthogonal axes

  - $(1 / d^2_{hkl}) = (h^2/a^2) + (k^2/b^2) + (l^2/c^2)$

- Hexagonal unit cells

  - $(1 / d^2_{hkl}) = (4/3)([h^2 + k^2 + hk]/ a^2) + (l^2/c^2)$

Crystal Structure Analysis

X-ray diffraction

Essence of diffraction: Bragg Diffraction

Light

Interference fringes

Constructive
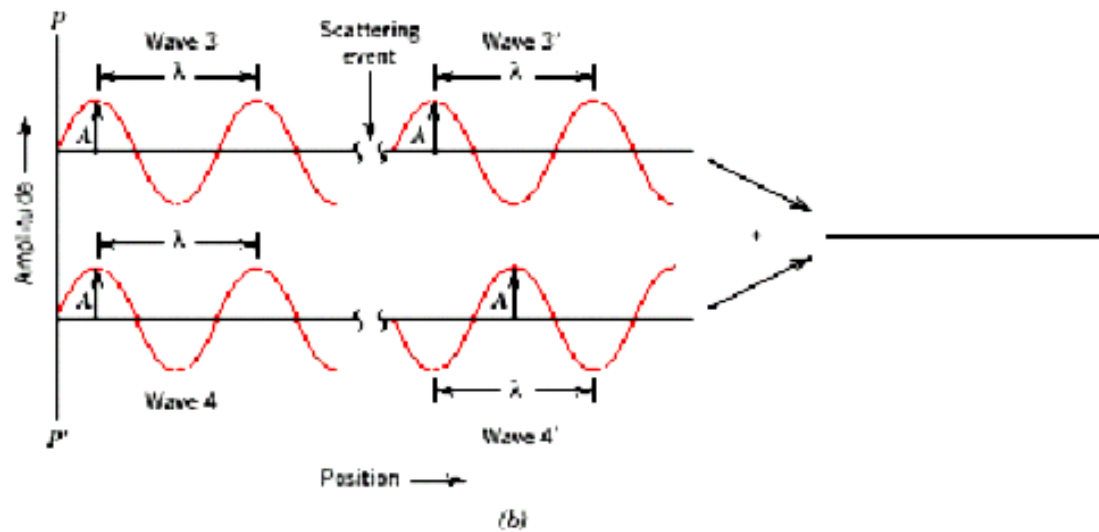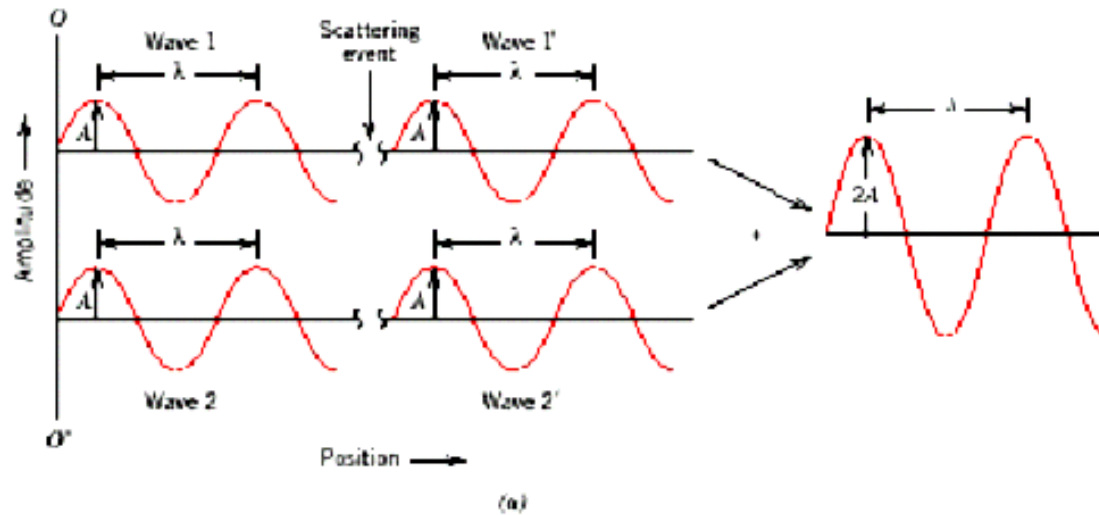
Destructive

Bragg's Law

$$n\lambda = \overline{SQ} + \overline{QT}$$

$$= d_{hkl}\sin\theta + d_{hkl}\sin\theta$$

$$= 2d_{hkl}\sin\theta$$
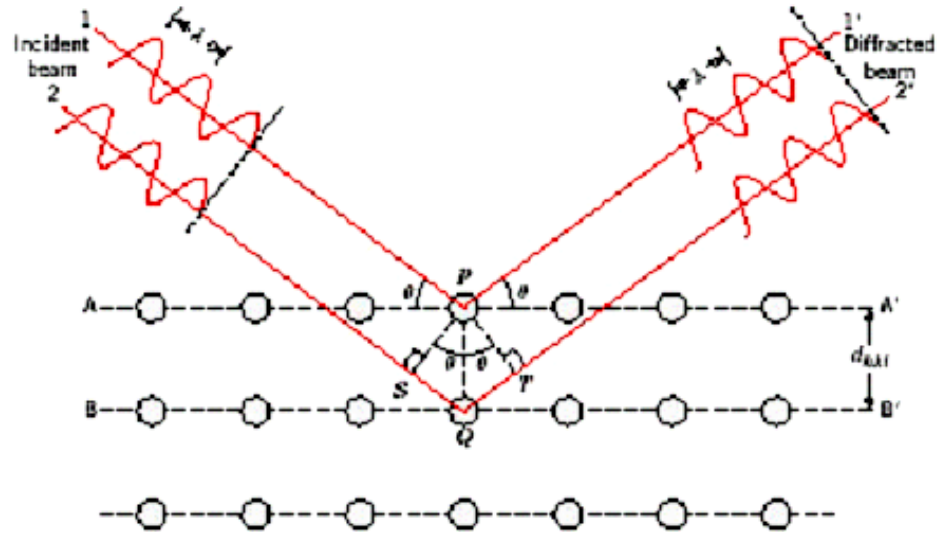
For cubic system:

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

But no all planes have the diffraction !!!

X-Ray Diffraction

- X-ray diffraction from a crystal: *Bragg's Law*

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

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

n: order of diffraction peak

d_{hkl}: interplanar spacing

(hkl): Miller indices of plane
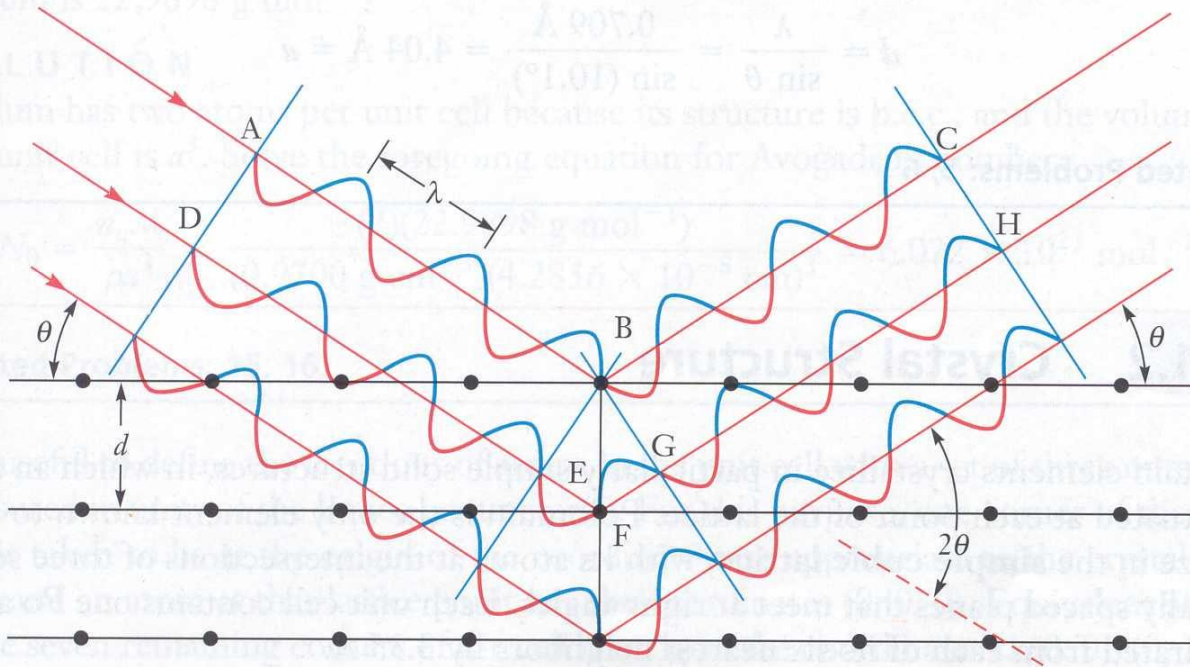
FIGURE 21.11 Constructive interference of x-rays scattered by atoms in lattice planes. Three beams of x-rays, scattered by atoms in three successive layers of a simple cubic crystal, are shown. Note that the phases of the waves are the same along the line CH, indicating constructive interference at this scattering angle 2θ.
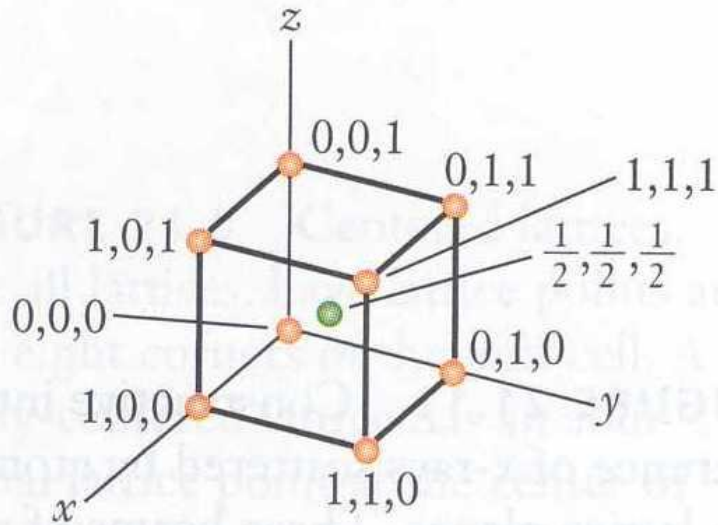
Crystal Structures [OGN 21.2]
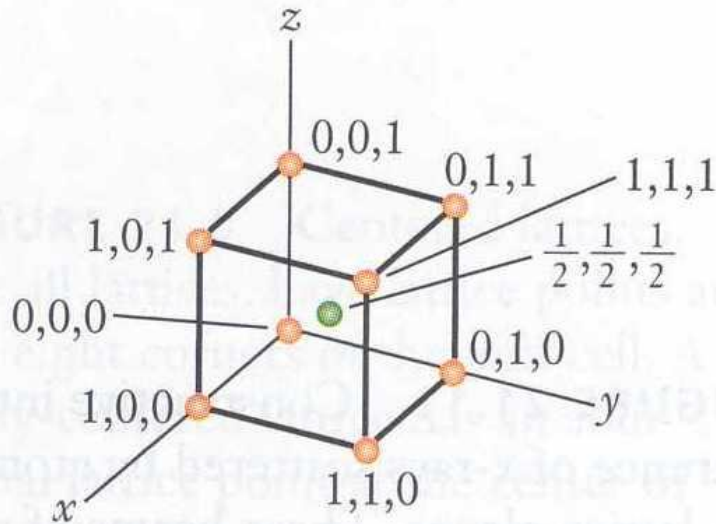
- Body-centered cubic

FIGURE 21.12 The b.c.c. structure. An atom is located at the center of each cubic cell (green) as well as at each corner of the cube (orange). The atoms are reduced slightly in size to make positions clear.
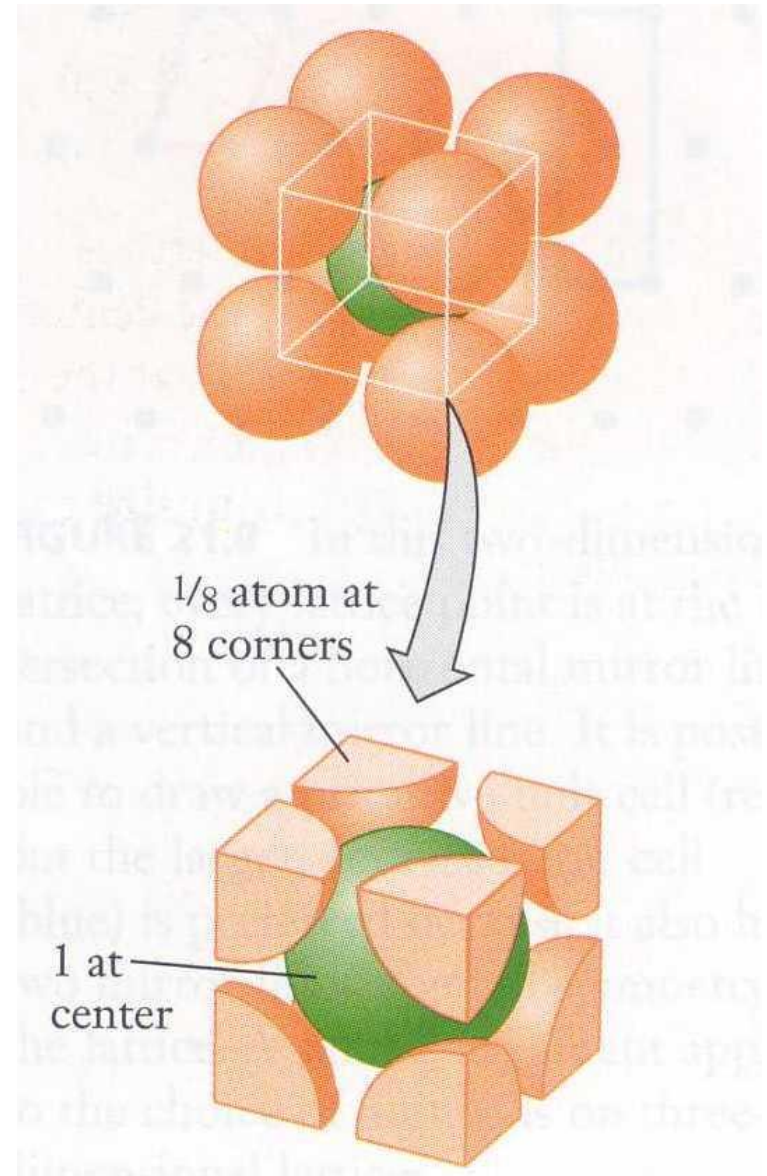
Single Crystal Diffraction

Diffracted Beam

Incident Beam

Powder Diffraction

Diffracted Beam

Incident Beam
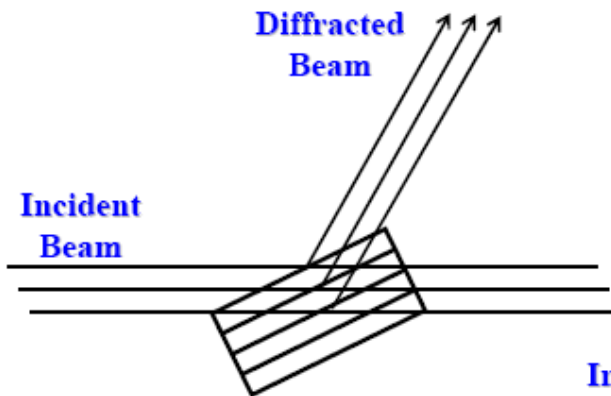
In powder diffraction only a small fraction of the crystals (shown in blue) are correctly oriented to diffract.
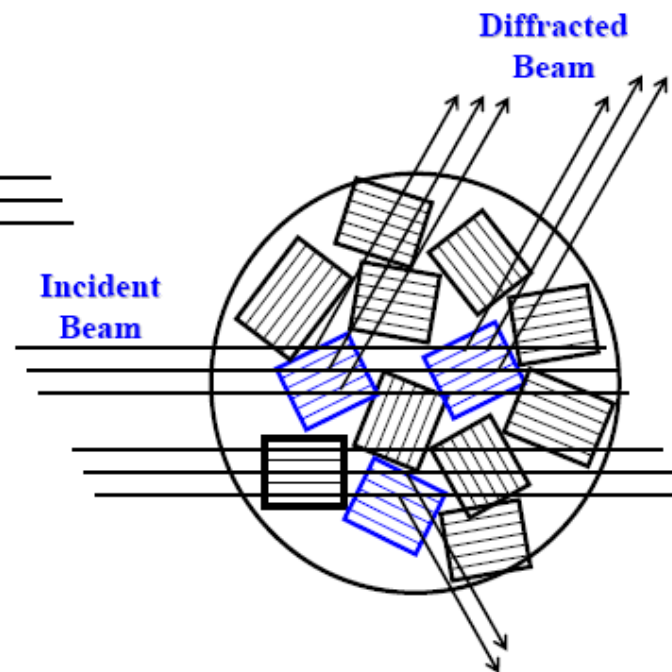
Information in a Diffraction Pattern

- **Peak Positions**
  - The peak positions tell you about the translational symmetry. Namely what is the size and shape of the unit cell.

- **Peak Intensities**
  - The peak intensities tell you about the electron density inside the unit cell. Namely where the atoms are located.

- **Peak Shapes & Widths**
  - The peak widths and shapes can give information on deviations from a perfect crystal. You can learn about the crystallite size if it is less than roughly 100 – 200 nm. You can also learn about extended defects and microstrain.

X-Ray Diffraction

$$E = h\nu = hc / \lambda$$
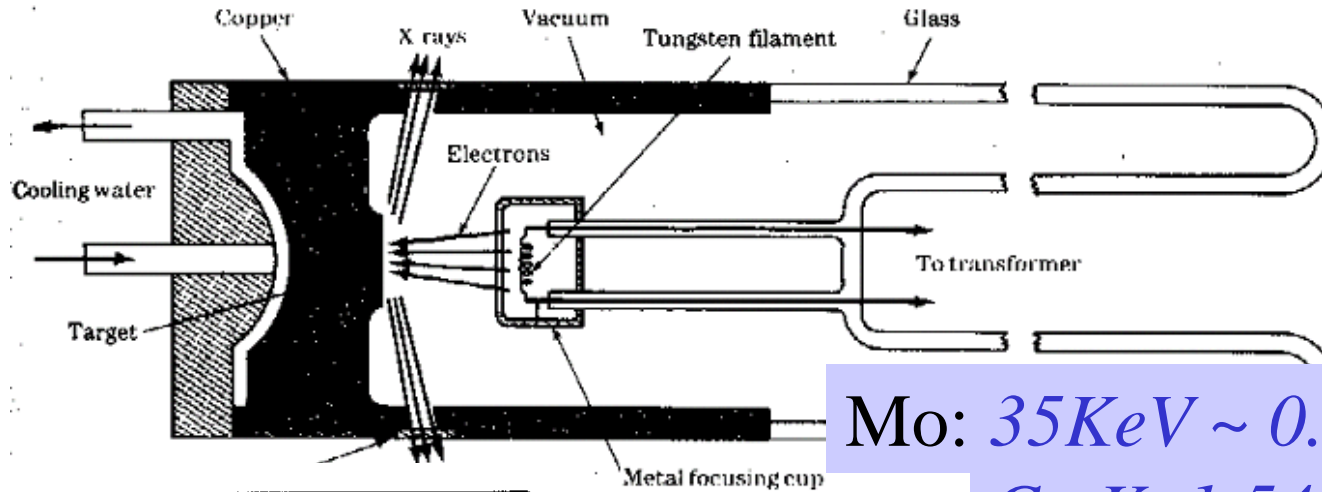
Mo: *35KeV ~ 0.1-1.4Å°*
Cu K 1.54 A
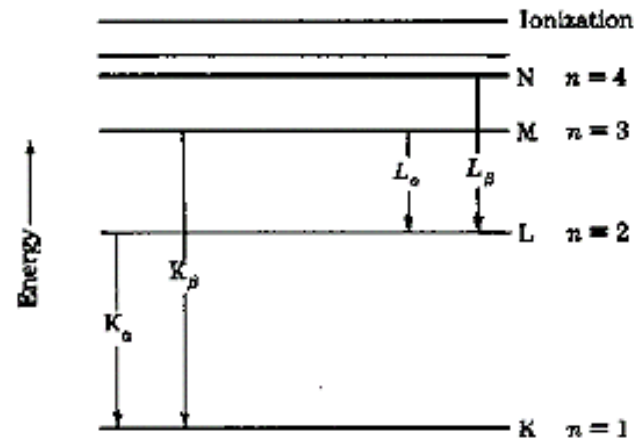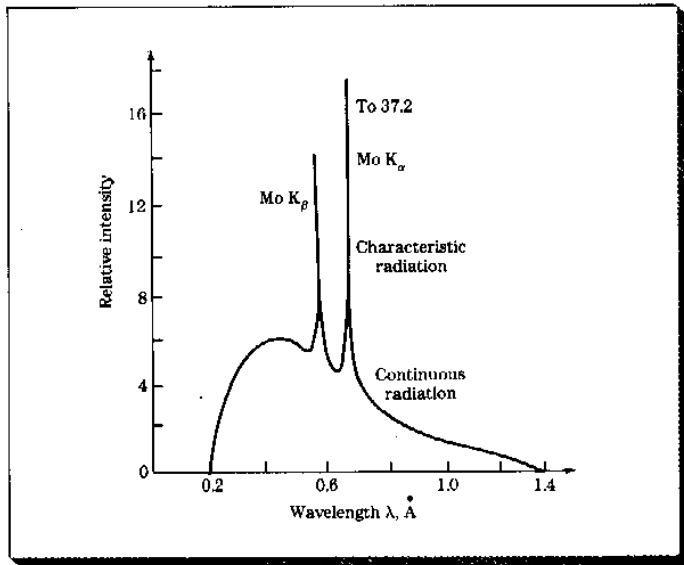
Powder diffraction
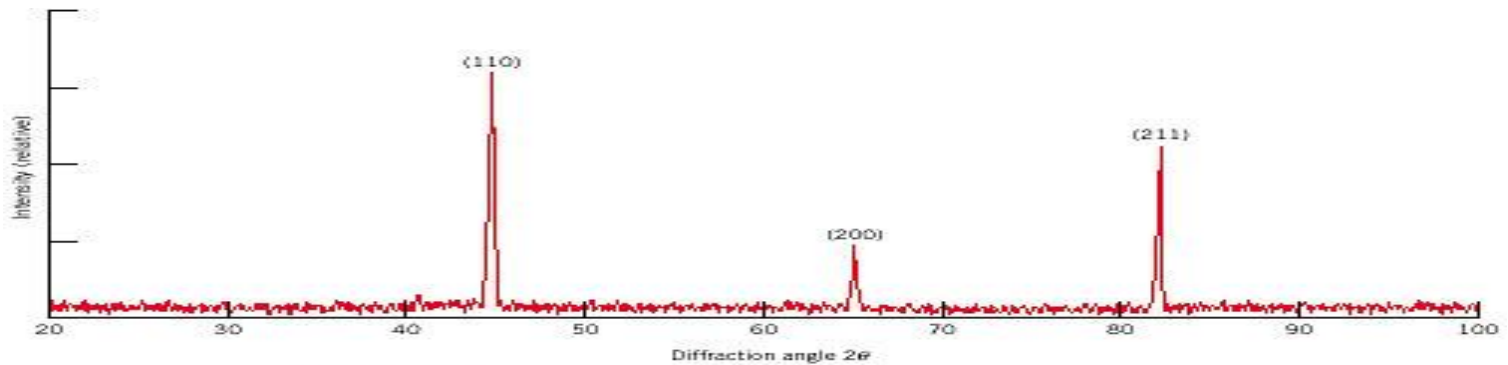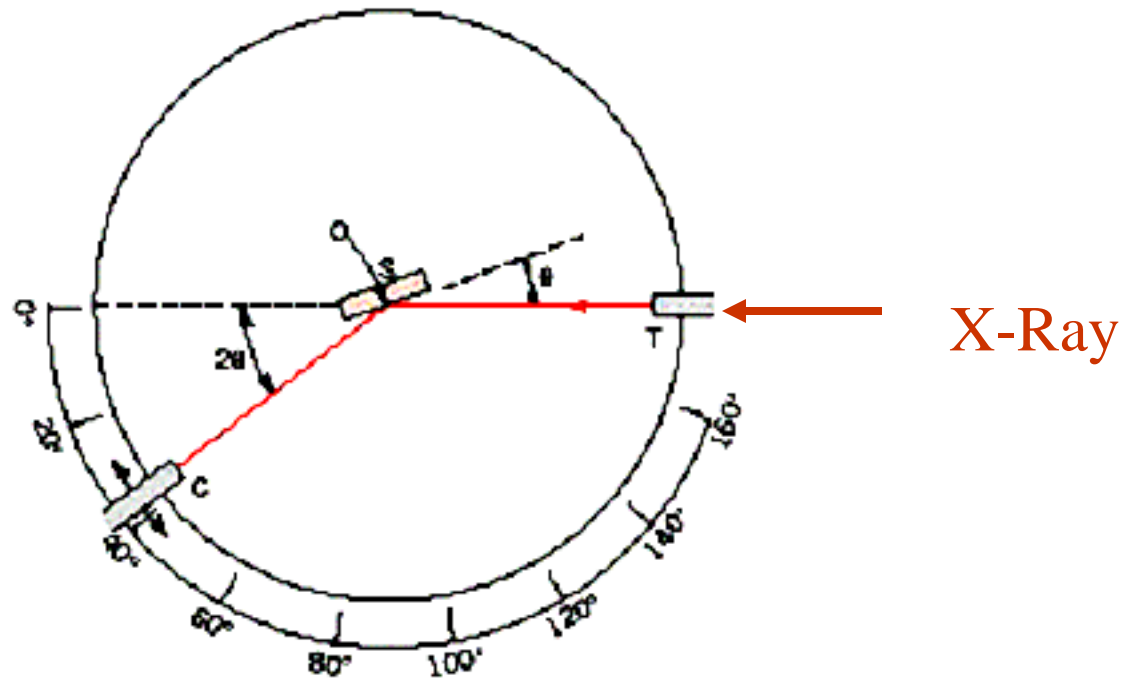
X-Ray

FIGURE 3.20   Diffraction pattern for polycrystalline α-iron.

Phase purity.

In a mixture of compounds each crystalline phase present will contribute to the overall powder X-ray diffraction pattern. In preparative materials chemistry this may be used to identify the level of reaction and purity of the product. The reaction between two solids Al_2O_3 and MgO to form $MgAl_2O_4$ may be monitored by powder X-ray diffraction.
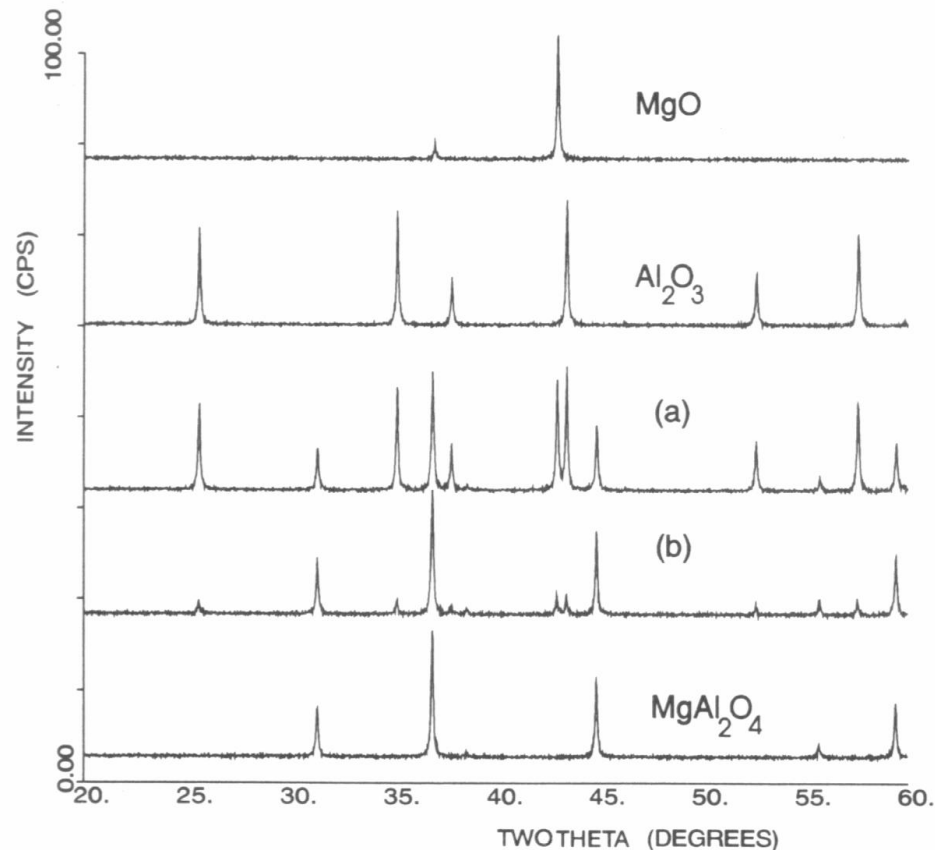
•At the start of the reaction a mixture of Al_2O_3 and MgO will produce an X-ray pattern combining those of the pure phases. As the reaction proceeds, patterns (a) and (b), a new set of reflections corresponding to the product $MgAl_2O_4$, emerges and grows in intensity at the expense of the reflection from Al_2O_3 and MgO. On completion of the reaction the powder diffraction pattern will be that of pure $MgAl_2O_4$.

•A materials chemist will often use PXRD to monitor the progress of a reaction.

•The PXRD method is widely employed to identify impurities in materials whether it be residual reactant in a product, or an undesired by-product.

•However the impurity **must** be crystalline.
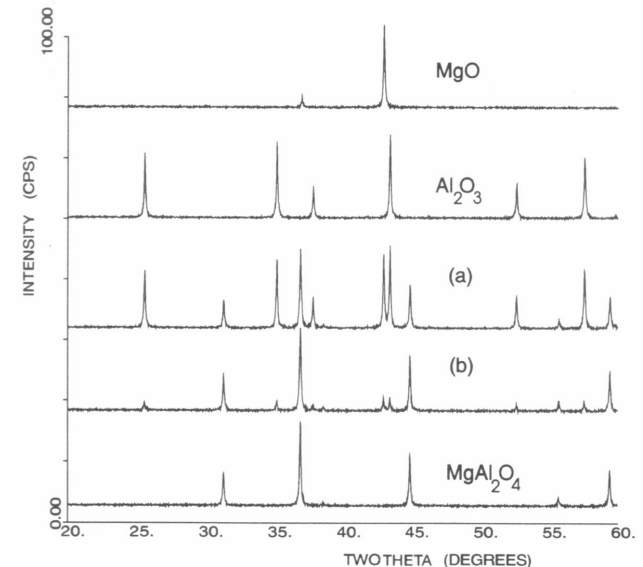
Face-centred cubic
h,k,l all even or all odd are present

Body-centred cubic
$h + k + l$ = odd are absent

Primitive cubic

(100)
(110)
(111)
(200)
(210)
(211)
(220)
(221), (300)
(310)
(311)
(221)
(320)
(321)
(400)
(410), (322)
(411), (330)
(331)
(420)
(421)
(441)
(332)
(422)
(502), (430)
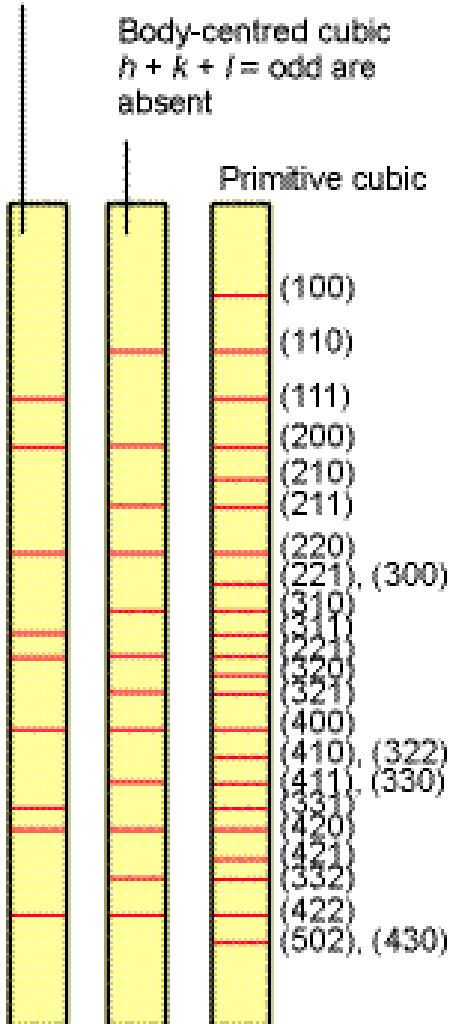
The powder diffraction patterns and the systematic absences of three versions of a cubic cell. Comparison of the observed pattern with patterns like these enables the unit cell to be identified. The locations of the lines give the cell dimensions.

Rules for Determining the Diffracting {hkl} Planes in Cubic Crystals

Bravais lattice	Reflections present	Reflections absent
BCC	$(h + k + l)$ = even	$(h + k + l)$ = odd
FCC	(h, k, l) all odd or all even	(h, k, l) not all odd or all even

Observable diffraction peaks

$$h^2 + k^2 + l^2$$

Ratio

SC: 1,2,3,4,5,6,8,9,10,11,12..

BCC: 2,4,6,8,10, 12….

FCC: 3,4,8,11,12,16,24….

Miller Indices of the Diffracting Planes for BCC and FCC Lattices

Cubic planes {hkl}	$h^2 + k^2 + l^2$	Sum $\Sigma(h^2 + k^2 + l^2)$	Cubic diffracting planes {hkl} FCC	BCC
{100}	$1^2 + 0^2 + 0^2$	1		
{110}	$1^2 + 1^2 + 0^2$	2	. . .	110
{111}	$1^2 + 1^2 + 1^2$	3	111	
{200}	$2^2 + 0^2 + 0^2$	4	200	200
{210}	$2^2 + 1^2 + 0^2$	5		
{211}	$2^2 + 1^2 + 1^2$	6	. . .	211
{220}	$2^2 + 2^2 + 0^2$	8	220	220
{221}	$2^2 + 2^2 + 1^2$	9		
{310}	$3^2 + 1^2 + 0^2$	10	. . .	310

Simple cubic

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

$$2d \sin \theta = n\lambda$$

Example: $SrTiO_3$

The crystal structure of $SrTiO_3$ is cubic, space group *Pm3m* with a unit cell edge a = 3.90 Å. Calculate the expected 2θ positions of the first three peaks in the diffraction pattern, if the radiation is Cu Kα (λ = 1.54 Å).

1. Recognize the hkl values for the first few peaks:

    100, 110, 111, 200, 210, 211, 220, etc.

2. Calculate the interplanar spacing, d, for each peak:

$$1/d^2 = (h^2 + k^2 + l^2)/a^2$$

3. Use Bragg's Law to determine the 2θ value:

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

Example: $SrTiO_3$

$hkl = 100$

$1/d^2 = (1^2 + 0^2 + 0^2)/(3.90 \text{ Å})^2 \quad \rightarrow \quad d = 3.90 \text{ Å}$

$\sin \theta_{100} = 1.54 \text{ Å}/\{2(3.90 \text{ Å})\} \quad \rightarrow \quad \theta = 11.4° \ (2\theta = 22.8°)$

$hkl = 110$

$1/d^2 = (1^2 + 1^2 + 0^2)/(3.90 \text{ Å})^2 \quad \rightarrow \quad d = 2.76 \text{ Å}$

$\sin \theta_{100} = 1.54 \text{ Å}/\{2(2.76 \text{ Å})\} \quad \rightarrow \quad \theta = 16.2° \ (2\theta = 32.4°)$

$hkl = 111$

$1/d^2 = (1^2 + 1^2 + 1^2)/(3.90 \text{ Å})^2 \quad \rightarrow \quad d = 2.25 \text{ Å}$

$\sin \theta_{100} = 1.54 \text{ Å}/\{2(2.25 \text{ Å})\} \quad \rightarrow \quad \theta = 20.0° \ (2\theta = 40.0°)$

Indexing

- Indexing is the process of determining the unit cell dimensions from the peak positions. To index a powder diffraction pattern it is necessary to **assign Miller indices, *hkl*, to each peak**.

- A diffraction pattern cannot be analyzed until it has been indexed. **It is always the first step in analysis**.

- Unfortunately it is not just the simple reverse of calculating peak positions from the unit cell dimensions and wavelength.

- We will show how one can manually index diffraction patterns of high symmetry structures. For lower symmetry structures (orthorhombic, monoclinic, triclinic) it is usually necessary to use a computer algorithm. **This is called Autoindexing**.

Indexing a Cubic Pattern

Bragg's Law tells us the location of a peak with indices hkl, θ_{hkl}, is related to the interplanar spacing, d, as follows:

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

$$1/d = 2 \sin \theta / \lambda$$

$$1/d^2 = 4 \sin^2 \theta / \lambda^2$$

Earlier we saw that for a cubic phase the d-values can be calculated from the Miller indices (hkl)

$$1/d^2 = (h^2 + k^2 + l^2)/a^2$$

Combining these two equations we get the following relationship

$$\sin^2 \theta / (h^2 + k^2 + l^2) = \lambda^2 / 4a^2$$

Need to find values of h,k,l for that give a constant when divided by each $\sin^2 \theta$.

Cubic Example

2-Theta	1000 sin²θ	1000 sin²θ /CF	hkl
22.21	37.1		
31.61	74.2		
38.97	111		
45.31	148		
51.01	185		
56.29	222		
66.00	297		
70.58	334		
75.03	371		
79.39	408		

We need to find a common factor, CF, that can be divided into each of the values in the second column to give an integer = $h^2+k^2+l^2$

CF = 37.1

2-Theta	$1000 \sin^2\theta$	$1000 \sin^2\theta$ /CF	hkl
22.21	37.1	1.00	
31.61	74.2	2.00	
38.97	111	2.99	
45.31	148	3.99	
51.01	185	4.99	
56.29	222	5.98	
66.00	297	8.01	
70.58	334	9.00	
75.03	371	10.00	
79.39	408	11.00	

$CF = (37.1/1000) = \lambda^2/4a^2 \rightarrow (a = 4.00\ A)$

2-Theta	$1000\ \sin^2\theta$	$1000\ \sin^2\theta\ /CF$	hkl
22.21	37.1	1.00	1 0 0
31.61	74.2	2.00	1 1 0
38.97	111	2.99	1 1 1
45.31	148	3.99	2 0 0
51.01	185	4.99	2 1 0
56.29	222	5.98	2 1 1
66.00	297	8.01	2 2 0
70.58	334	9.00	300/221
75.03	371	10.00	3 1 0
79.39	408	11.00	3 1 1

Ex: An element, BCC or FCC, shows diffraction peaks at 2θ:
40, 58, 73, 86.8,100.4 and 114.7.
Determine:(a) Crystal structure?(b) Lattice constant?
(c) What is the element?

2theta	theta	$\sin^2\theta$	$h^2 + k^2 + l^2$	(hkl)
40	20	0.117	1	(110)
58	29	0.235	2	(200)
73	36.5	0.3538	3	(211)
86.8	43.4	0.4721	4	(220)
100.4	50.2	0.5903	5	(310)
114.7	57.35	0.7090	6	(222)

a =3.18 A, BCC, → W

Autoindexing Software

A number of the most useful autoindexing programs have been gathered together by Robin Shirley into a single package called **Crysfire**. You can download Crysfire from the web and find tutorials on its use at

http://www.ccp14.ac.uk/tutorial/crys/index.html

To go index a powder diffraction pattern try the following steps:

- Fit the peaks using a program such as X-Fit (http://www.ccp14.ac.uk/tutorial/xfit-95/xfit.htm)

- Take the X-fit output file and convert to a Crysfire input file, as described on the web.

- Run Crysfire to look for the best solutions.

- Evaluate the systematic absences and refine the cell parameters. This can be done using the material in the front of the international tables for crystallography or using a program like Chekcell (http://www.ccp14.ac.uk/tutorial/lmgp/index.html).