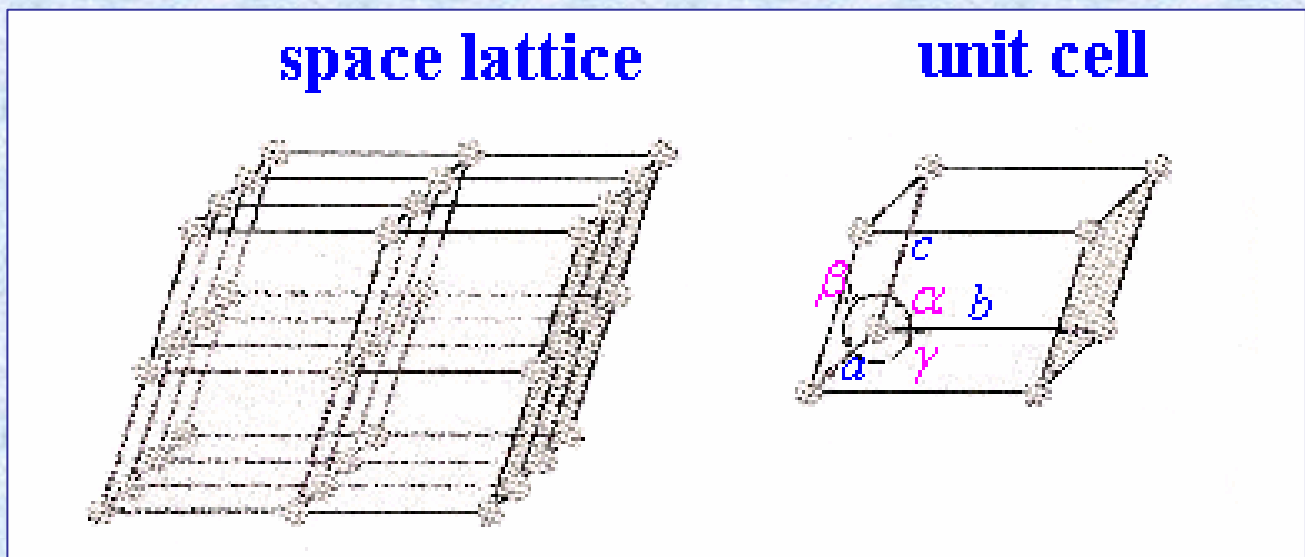# 2. Crystal Structure

crystalline solid – the atoms or ions arrange in a
    pattern that repeats itself in three dimensions
    to form a solid which has long-range order

amorphous solid – materials with only short-
    range order

space lattice – a network composed of an infinite
    three-dimensional array of points

unit cell – the repeating unit in a space lattice

lattice constants
   lattice vector – a, b, c
   interaxial angle – α, β, γ

crystal system

only 7 different types of unit cells
14 standard (Bravais) unit cells could
describe all possible lattice networks

| crystal system	axial lengths & interaxial angles	space lattice
cubic	$a = b = c$ $\alpha = \beta = \gamma = 90^o$	simple cubic body-centered cubic face-centered cubic
tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90^o$	simple tetragonal body-centered tetragonal
orthorhombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^o$	simple orthorhombic body-centered orthorhombic base-centered orthorhombic face-centered orthorhombic
rhombohedral	$a = b = c$ $\alpha = \beta = \gamma \neq 90^o$	simple rhombohedral
hexagonal	$a = b \neq c$ $\alpha = \beta = 90^o$ $\gamma = 120^o$	simple hexagonal
monoclinic	$a \neq b \neq c$ $\alpha = \gamma = 90^o \neq \beta$	simple monoclinic base-centered monoclinic
triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^o$	simple triclinic
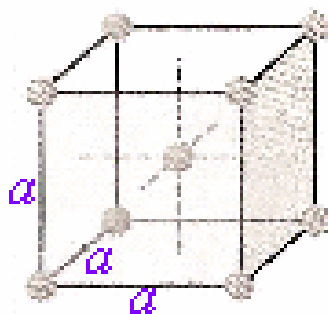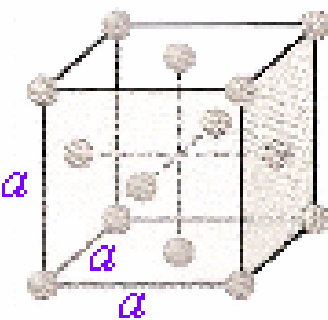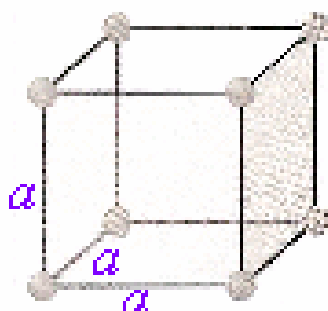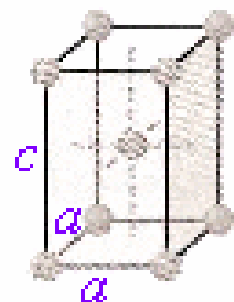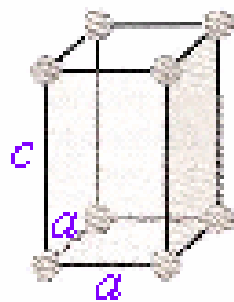
Cubic

Tetragonal
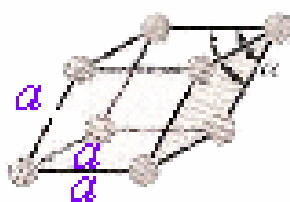
Rhombohedral
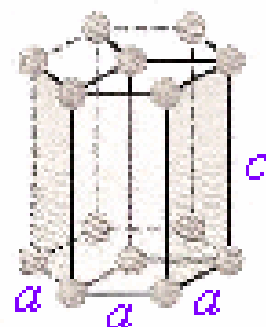
Hexagonal
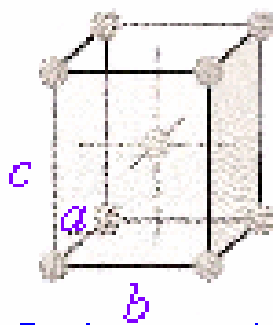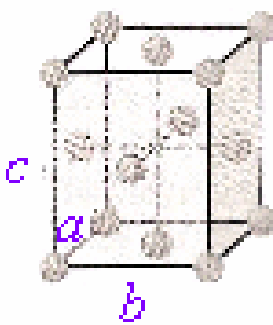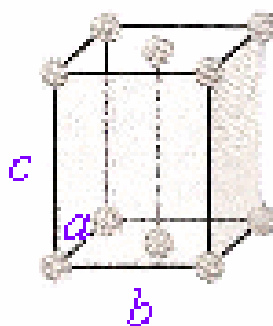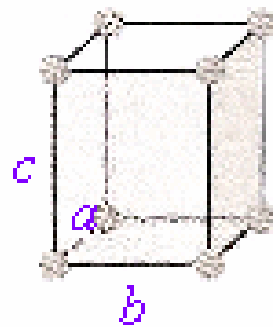
Orthorhombic

Monoclinic

Triclinic

3
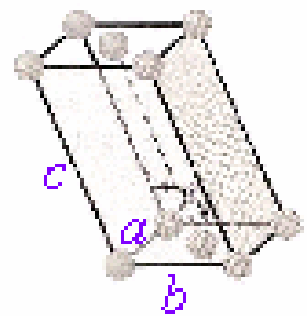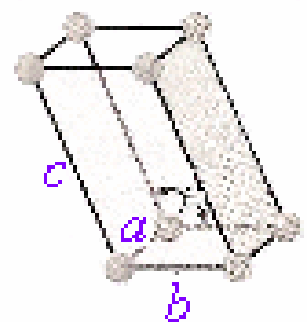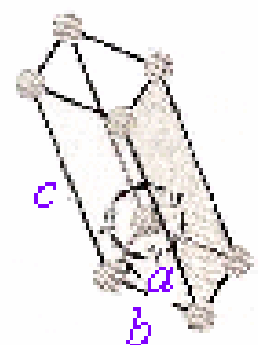
metallic crystal structures
90% elemental metals crystallize into three
crystal structures:

- **body-centered cubic** (BCC)

	a (nm)	R (nm)
Cr	0.289	0.125
Fe	0.287	0.124
Mo	0.315	0.136
K	0.533	0.231
Na	0.429	0.186
Ta	0.330	0.143
W	0.316	0.137
V	0.304	0.132

- **face-centered cubic** (FCC)

	a (nm)	R (nm)
Al	0.405	0.143
Cu	0.3615	0.128
Au	0.408	0.144
Pb	0.495	0.175
Ni	0.352	0.125
Pt	0.393	0.139
Ag	0.409	0.144

- **hexagonal close-packed** (HCP)

	a	c (nm)	R (nm)
Al	0.2973	0.5618	0.143
Zn	0.2665	0.4947	0.133
Mg	0.3209	0.5209	0.160
Co	0.2507	0.4069	0.125
Zr	0.3231	0.5148	0.160
Ti	0.2950	0.4683	0.147
Be	0.2286	0.3584	0.113
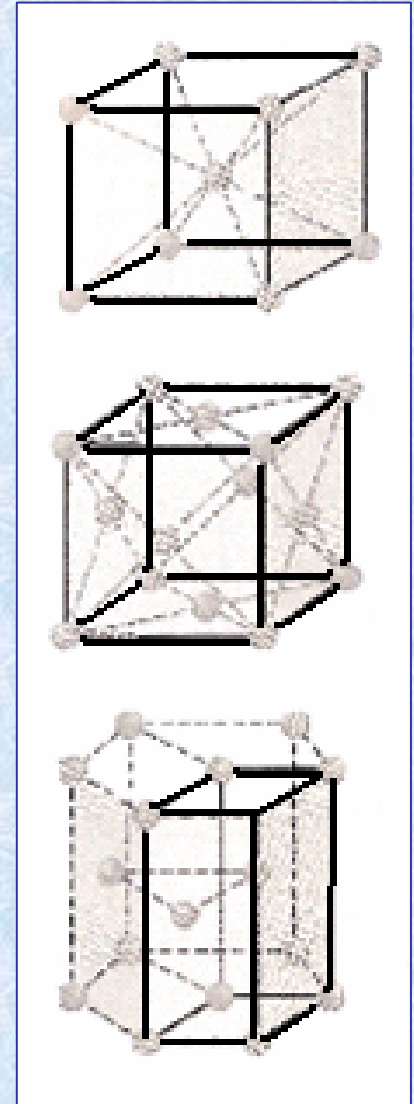
BCC
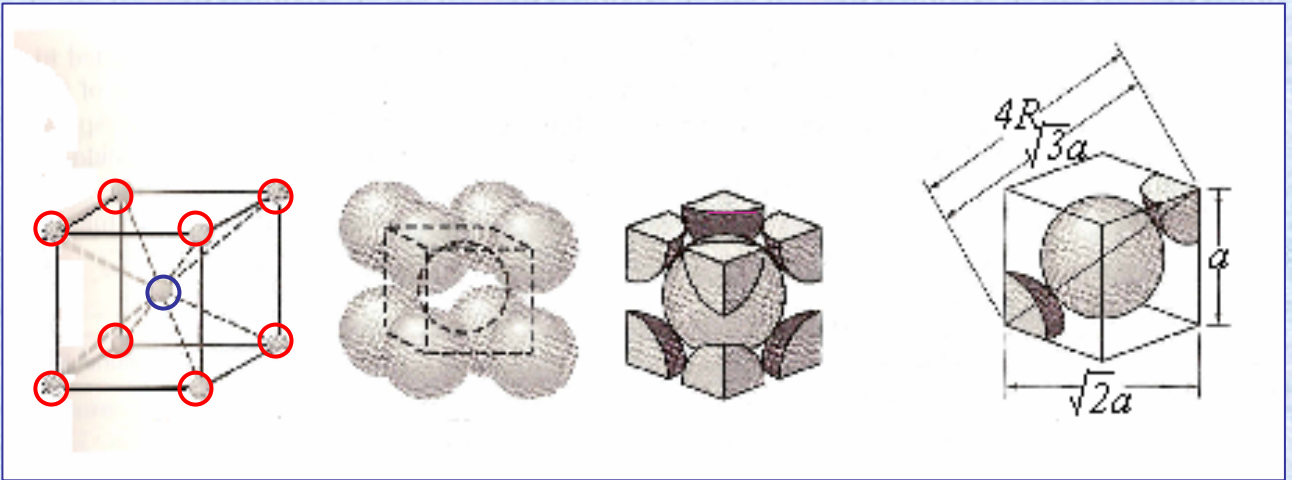
coordination number = 8
total 2 atoms per unit cell

$$\sqrt{3}\,a = 4\,R \qquad a = \frac{4\,R}{\sqrt{3}}$$

atomic packing factor (APF)
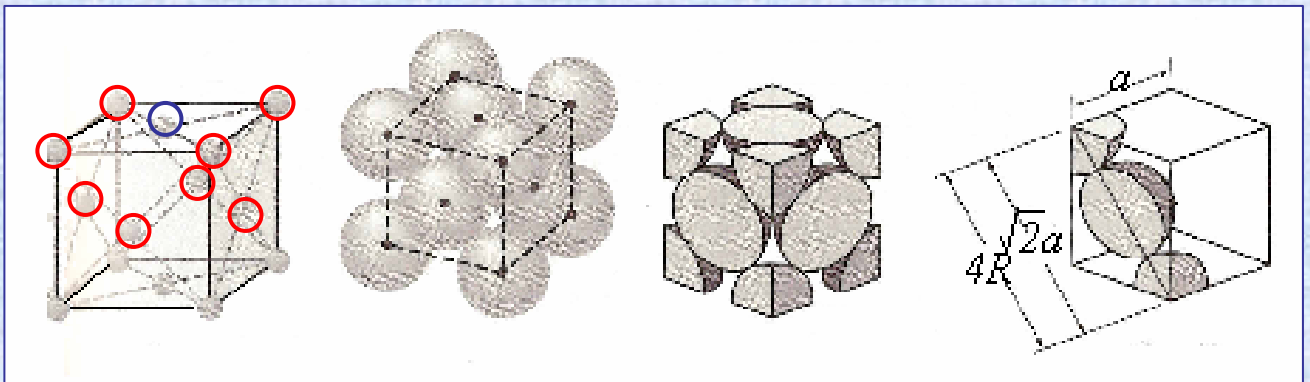
$$APF = \frac{\text{volume of atoms in unit cell}}{\text{volume of unit cell}}$$

APF = 0.68

FCC

coordination number = 12

total 4 atoms per unit cell
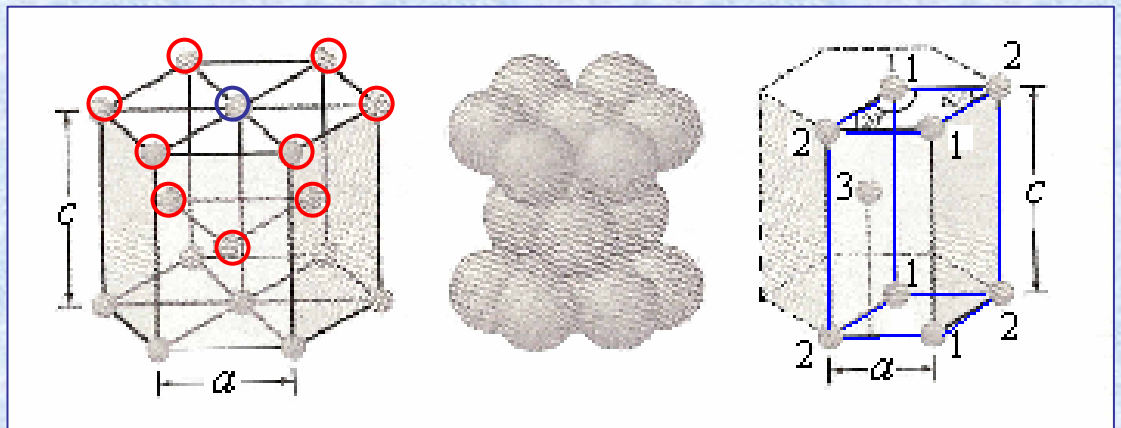
$$\sqrt{2}\, a = 4\,R \qquad a = \frac{4\,R}{\sqrt{2}}$$

APF = 0.74

the closest packing possible of spherical atoms cubic closest-packed
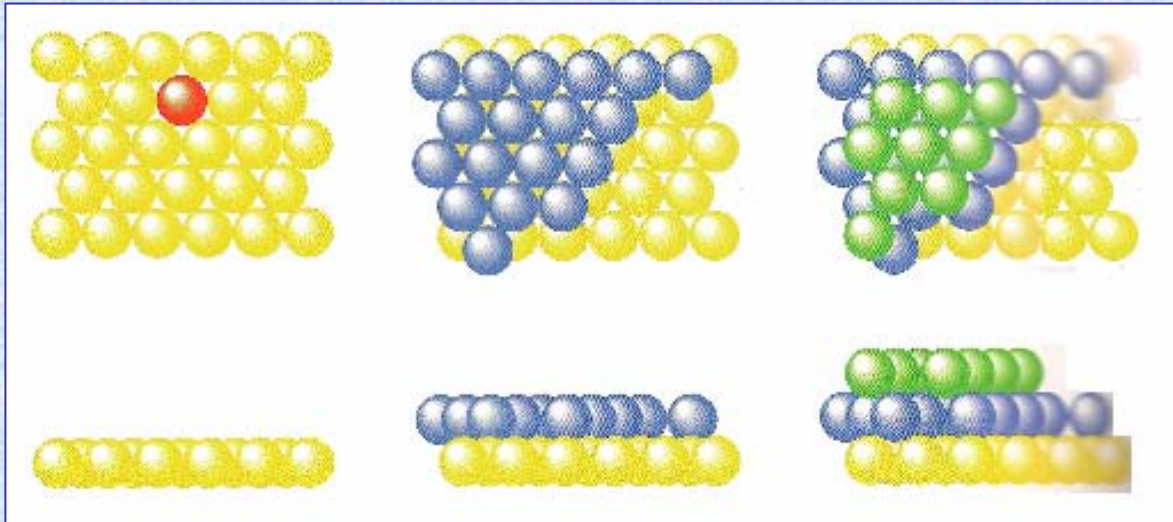
HCP

coordination number = 12
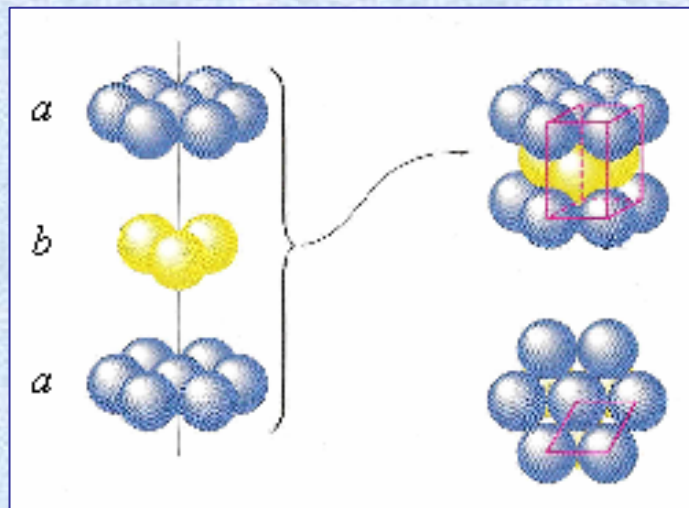
total 2 atoms per unit cell

APF = 0.74

the closest packing possible of spherical atoms

c/a ratio for ideal HCP structure is 1.633

the closest packing

HCP   *a b a b a* …..

FCC   *a b c a b c* ….
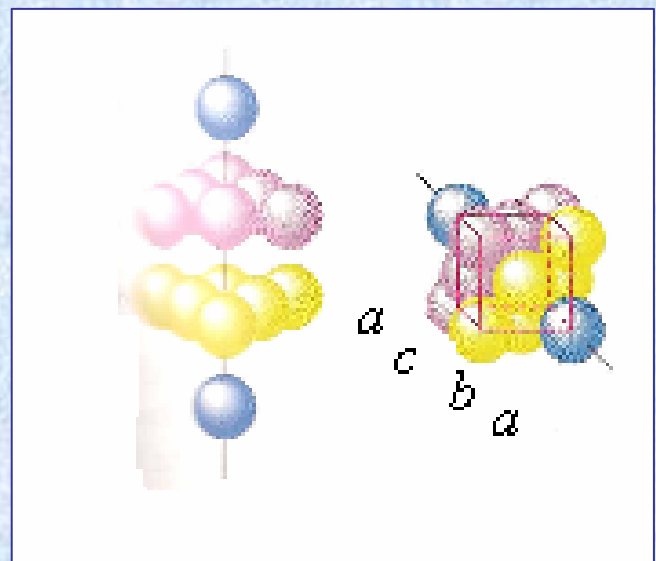
atom positions in cubic unit cell
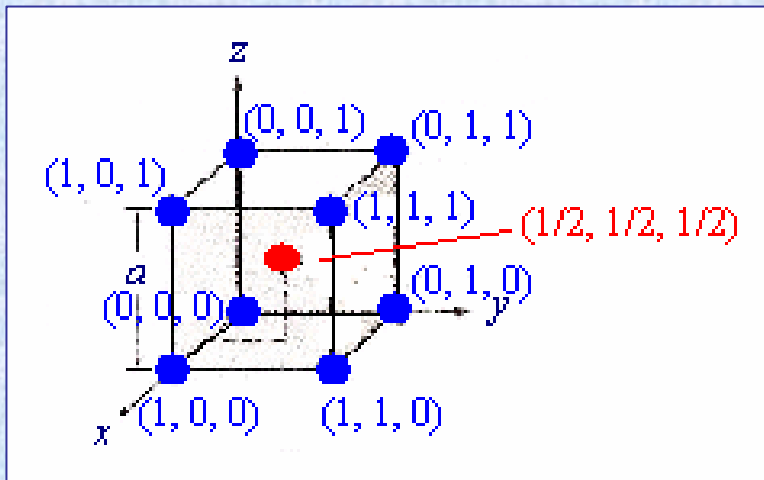
BCC unit cell
    coordinates of eight corners:
    (0, 0, 0)   (1, 0, 0)   (0, 1, 0)   (0, 0, 1)
    (1, 1, 0)   (1, 0, 1)   (0, 1, 1)   (1, 1, 1)
    coordinate of the center: (½, ½, ½)

direction index – the vector components of the
    direction resolved along each of the
    coordinate axes and reduced to the smallest
    integers

    all parallel direction vectors have the same
    direction indices

directions are crystallographically equivalent if the atom spacing along each direction is the same

ex. cubic edge directions:

$[100]$ $[010]$ $[001]$ $[0\bar{1}0]$ $[00\bar{1}]$ $[\bar{1}00]$
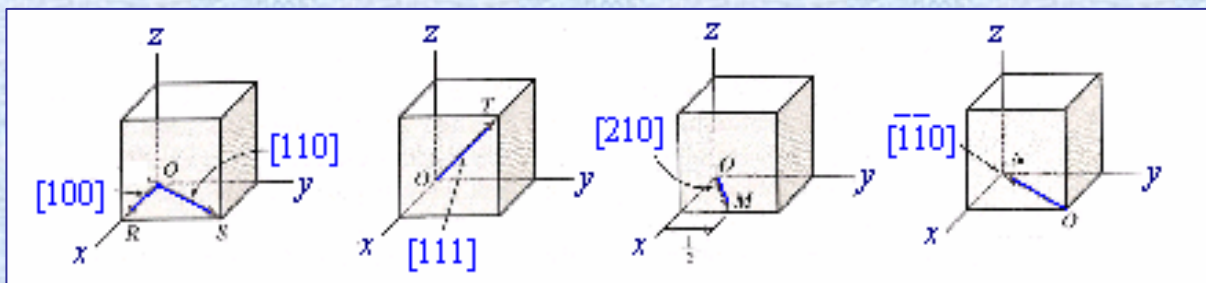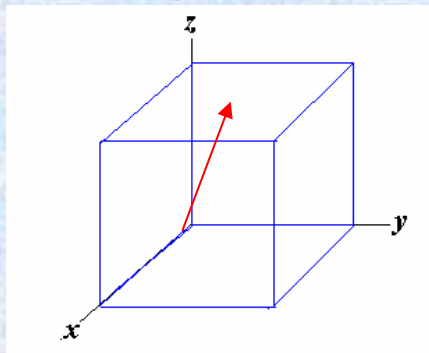
$\equiv$ <100>

equivalent directions are called indices of a family or form

ex. draw the following directions:

(a) [112]

(b) [$\bar{1}$10]
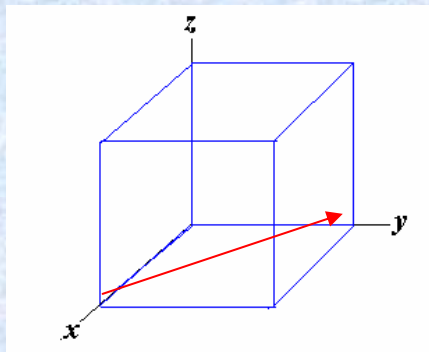
(c) [$\bar{3}2\bar{1}$]
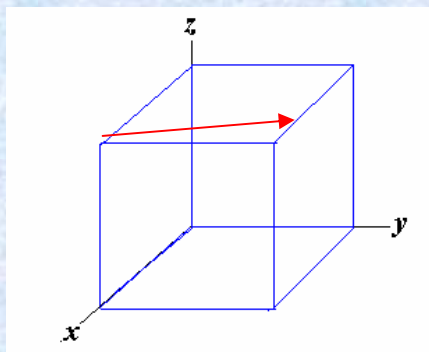
Miller indices for crystallographic planes
Miller notation system   (*hkl*)
Miller index – the reciprocals of the fractional
intercepts that the plane makes with the *x*, *y*,
and *z* axes of the three nonparallel edges of
the cubic unit cell
procedure for determining Miller index:
(1) choose a plane not pass through (0, 0, 0)
(2) determine the intercepts of the plane with
x, *y*, and *z* axes
(3) form the reciprocals of these intercepts
(4) find the smallest set of whole numbers
that are in the same ratio as the intercepts
ex.
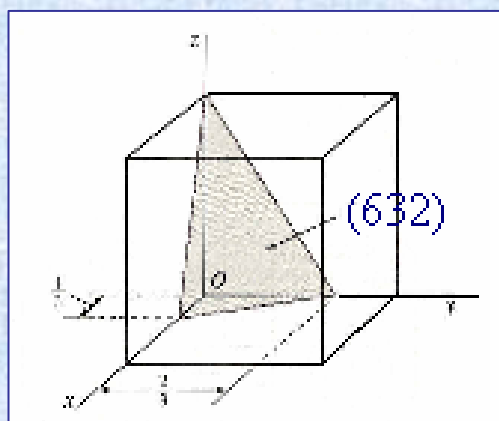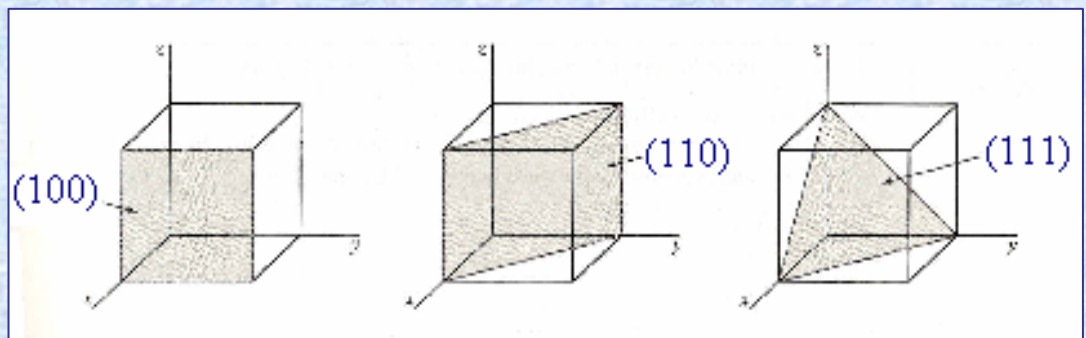
ex. draw the following crystallographic planes
   in cubic unit cell:
   (a) (101)   (b) (110)
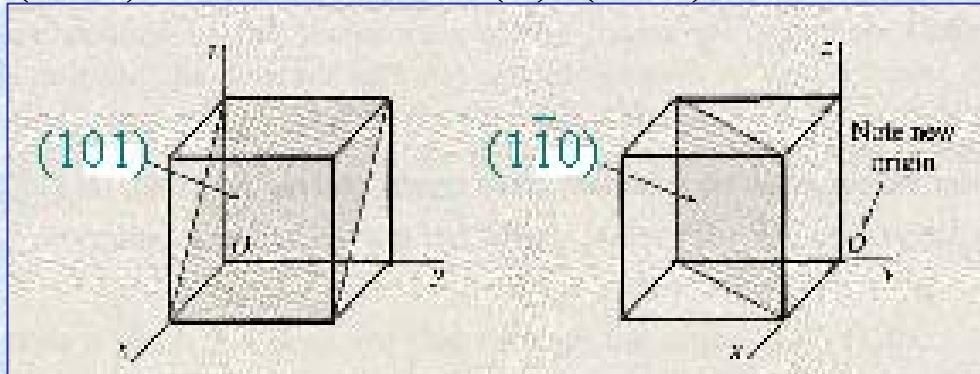
   (c) (221)
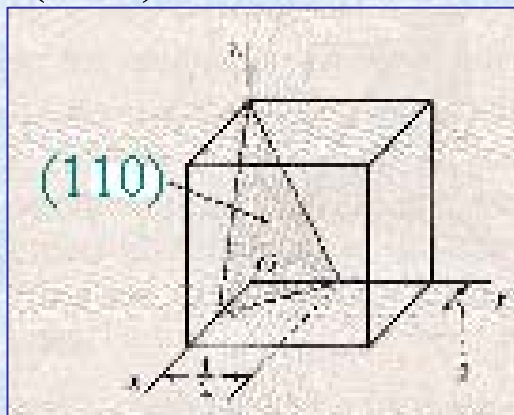
planes of a family or form   {hkl}
   ex. (100), (010), (001) are a family
              {100}

an important relationship for cubic system,
the direction indices of a direction perpendicular
to a crystal plane are the same as the Miller
indices of that plane

interplanar spacing between two closest parallel planes with the same Miller indices is designated d_{hkl} (*h, k, l* are the Miller indices)
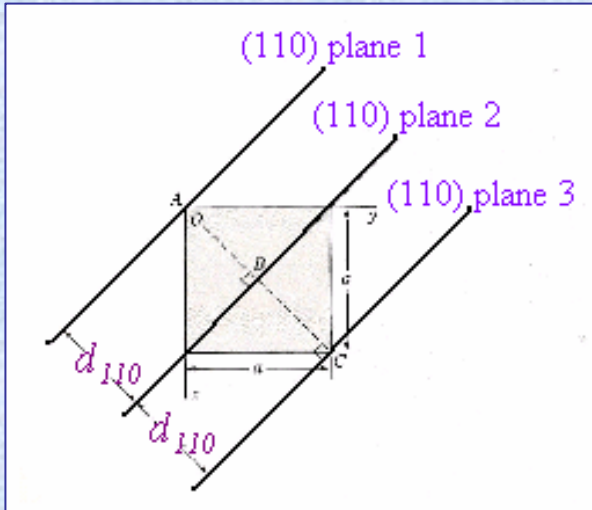
$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

a: = lattice constant

ex. determine the Miller indices of the planes shown as follow:

(a)

(5̄120)

(b)
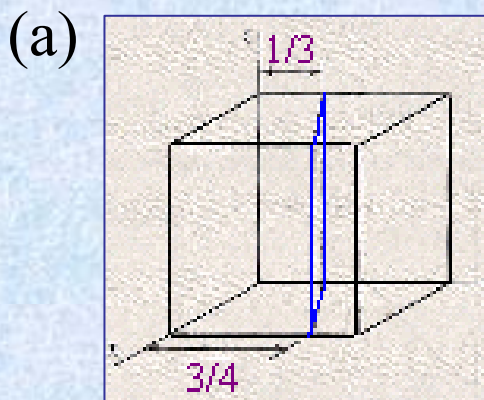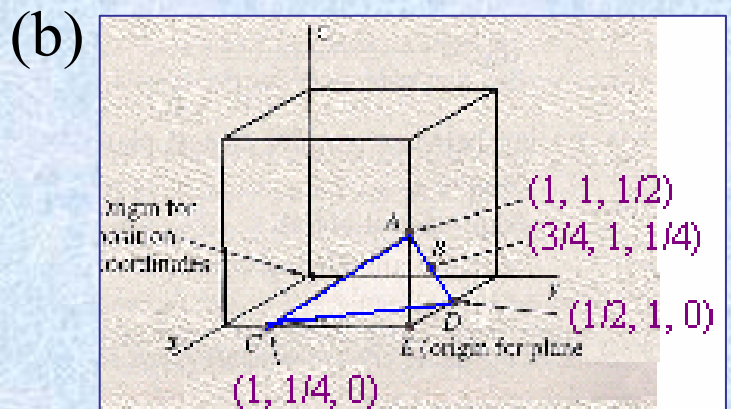
(6̄4̄6)

hexagonal structure

Miller-Bravais indices – HCP crystal plane indices ($hkil$) $h + k + i = 0$ three basal axes a_1, a_2, a_3 and c axis
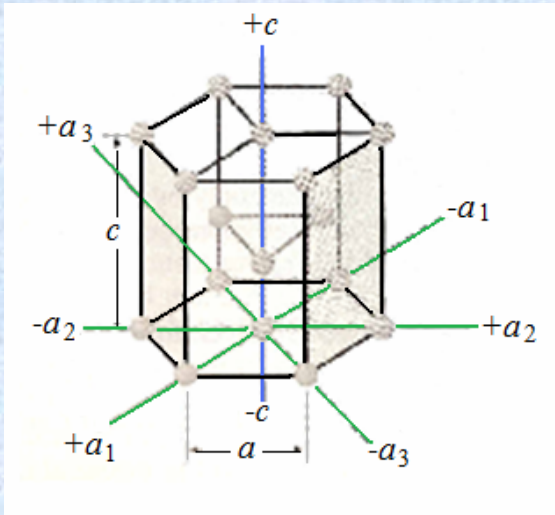
basal planes (0001)
prism planes
(ABCD) ($10\bar{1}0$)

(ABEF) ($1\bar{1}00$)

(CDGH) ($01\bar{1}0$)
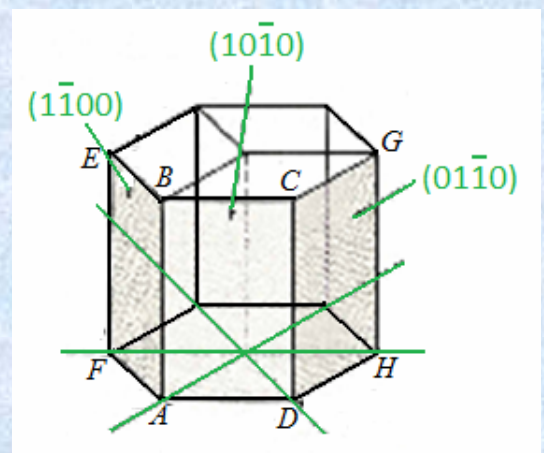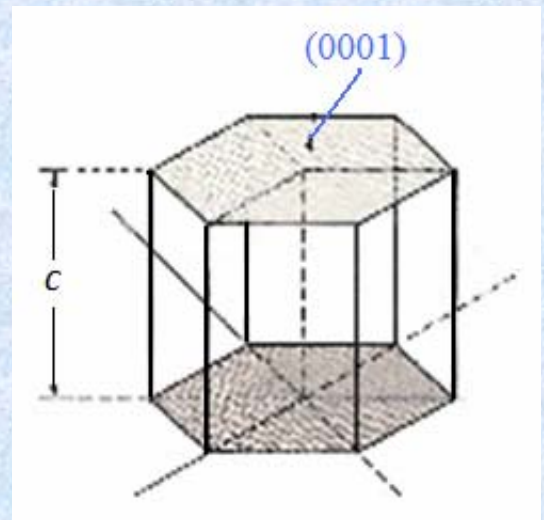
direction indices in HCP unit cell
　　four indices　　$[uvtw]$　　　　$u + v + t = 0$
　　　　$u = \tfrac{1}{3}(2u - v)$　　$v = \tfrac{1}{3}(2u - v)$　　$t = -(u + v)$
　　directions a_1, a_2, a_3
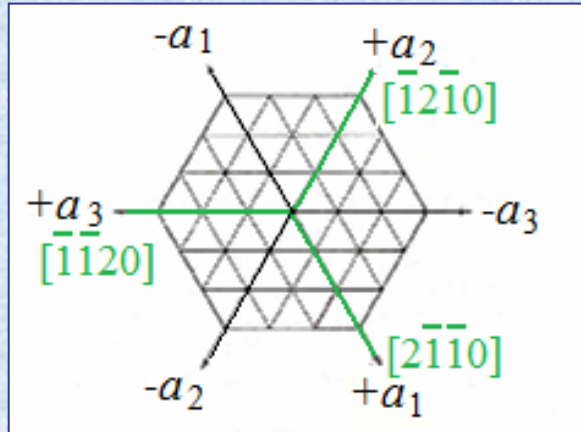
$+a_3$ direction incorporating c axis
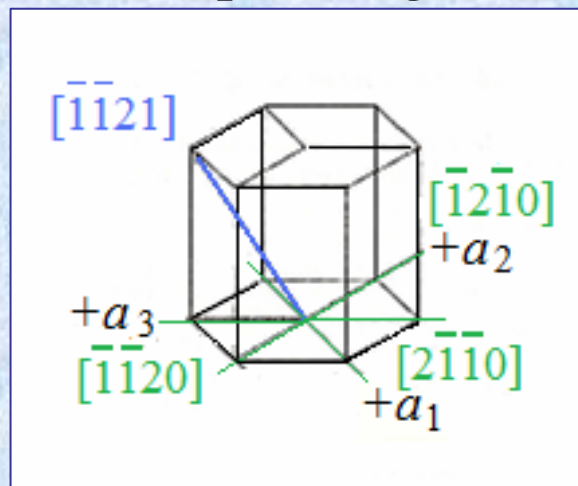
directions on the upper basal planes
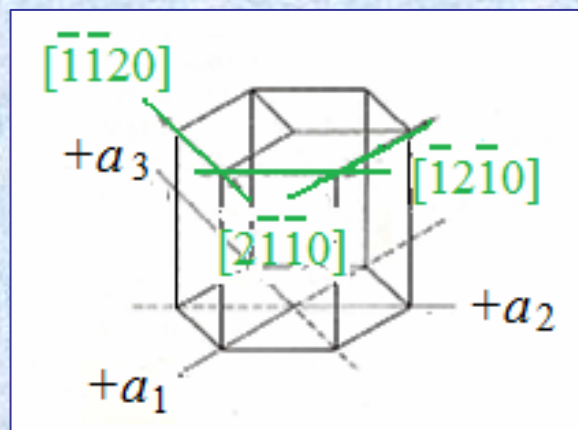
volume, planar, linear density

  volume density

$$\rho_v = \frac{\text{mass/unit cell}}{\text{volume/unit cell}}$$

ex. Cu has FCC structure, atomic radius of 0.1278 nm, atomic mass of 63.54 g/mol calculate the density of Cu in Mg/m^3.

FCC structure $\sqrt{2}\, a = 4\, R$

$a = 2\sqrt{2}\, R = 2\sqrt{2}\,(1.278 \times 10^{-10})$

$= 3.61 \times 10^{-10} m$

$V = (3.61 \times 10^{-10}\, m)^3 = 4.70 \times 10^{-29}\, m^3$

4 Cu per unit cell

$m = 4 \times 63.54 \times 1.66 \times 10^{-30}\, Mg = 4.22 \times 10^{-28}\, Mg$

$\rho_v = 4.22 \times 10^{-28}\, Mg\, /\, 4.70 \times 10^{-29}\, m^3$

$= 8.98\, Mg/m^3 \quad (\text{exp.} = 8.96\, Mg/m^3)$

planar atomic density

$$\rho_p = \frac{\text{equiv. no. of atoms whose centers are intersected by selected area}}{\text{selected area}}$$

ex. calculate planar atomic density ρ_p on (110) plane of the α-Fe in BCC lattice in $atoms/mm^2$. (lattice constant $a = 0.287$ nm)
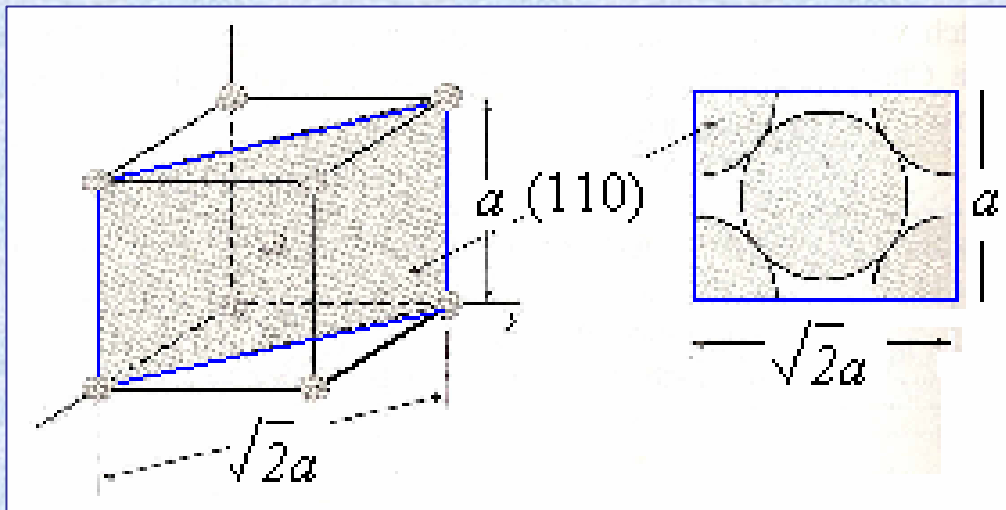
1 atom (center) + ¼ atom (corner) $\times$ 4 = 2 atoms

area = $a \times \sqrt{2}\, a = \sqrt{2}\, a^2 = \sqrt{2}\, (2.87 \times 10^{-7})^2$

$\qquad = 1.164 \times 10^{-13}$ mm^2

$$\rho_p = \frac{2 \text{ atoms}}{1.164 \times 10^{-13} \text{ mm}^2} = 1.72 \times 10^{13} \text{ atoms/mm}^2$$

linear atomic density

$$\rho_l = \frac{\text{no. of atoms diam. intersected by selected length of line in direction of interest}}{\text{selected length of line}}$$

ex. calculate linear atomic density ρ_l in [110] direction in Cu crystal lattice in atoms/mm. (Cu is FCC and lattice constant $a = 0.361$ nm)

no. of atoms = ½ + 1 + ½ = 2 atoms

length = $\sqrt{2}\,a = \sqrt{2}\,(3.61 \times 10^{-7})$

$= 5.104 \times 10^{-7}$ mm

$$\rho_l = \frac{2 \text{ atoms}}{5.104 \times 10^{-7} \text{ mm}} = 3.92 \times 10^6$$

[110]
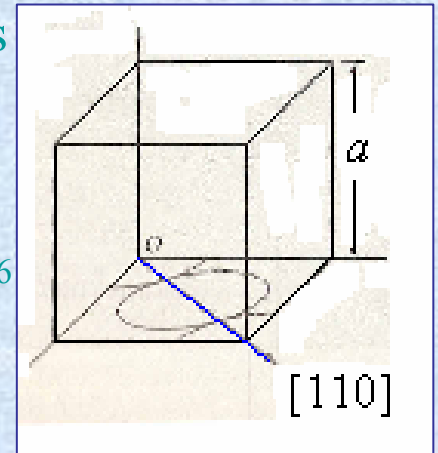
polymorphism or allotropy

element or compound exists in more than one crystalline form under different conditions of temperature and pressure

ex.

metal	crystal structure at room temperature	at other temperature
Ca	FCC	BCC (> 447°C)
Co	HCP	FCC (> 427°C)
Hf	HCP	BCC (> 1742°C)
Fe	BCC (α)	FCC (912-1394°C) (γ)
		BCC (> 1394°C) (δ)
Li	BCC	HCP (< -193°C)
Na	BCC	HCP (< -233°C)
Tl	HCP	BCC (> 234°C)
Ti	HCP	BCC (> 883°C)
Y	HCP	BCC (> 1481°C)
Zr	HCP	BCC (> 872°C)

crystal structure analysis

X-ray sources

x-rays used for diffraction are radiations with wavelengths 0.05 ~ 0.25 nm
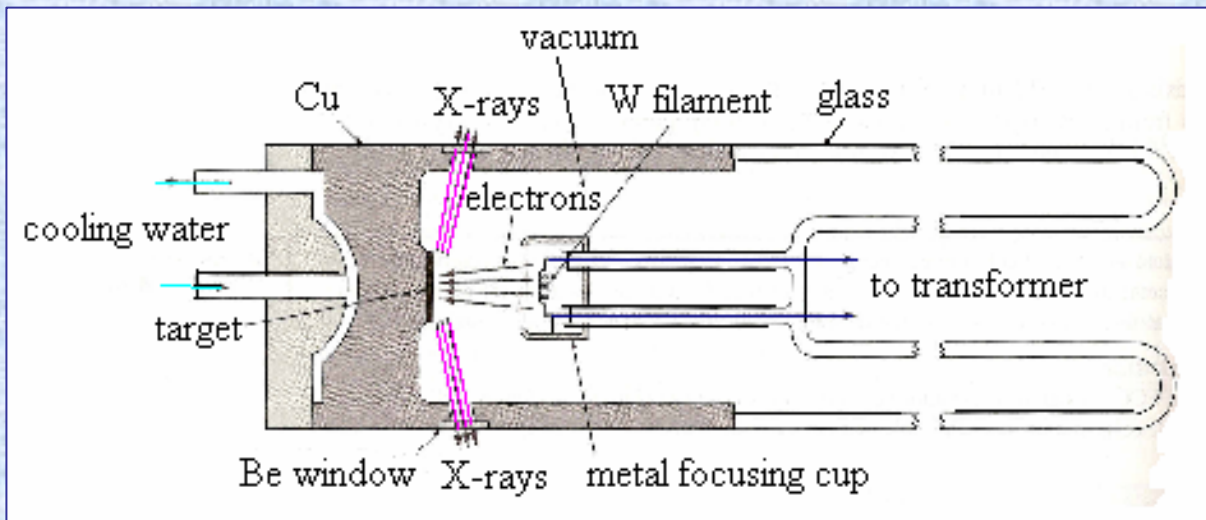
a voltage of 35 kV is applied between cathode (W filament) and anode (Mo target)

x-ray spectrum 0.2 ~ 1.4 nm

wavelength of K_α line 0.07 nm
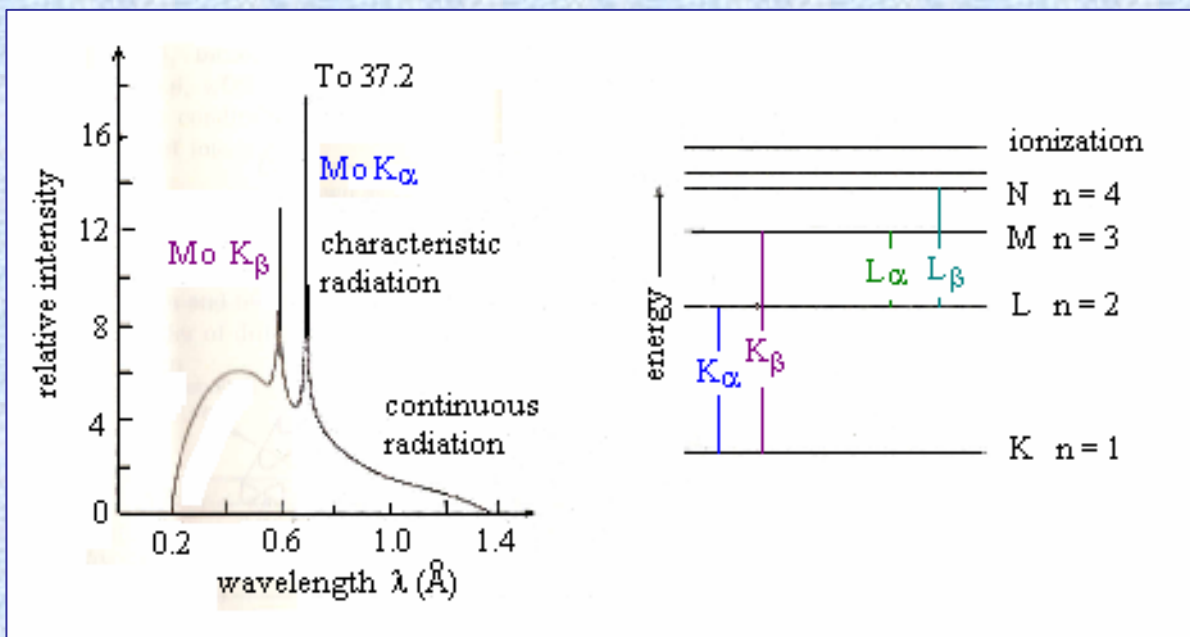
X-ray diffraction
reflected wave patterns of beam are not in phase,
no reinforced beam will be produced
destructive interference occurs

reflected wave patterns of beam are in phase,
reinforcement of the beam or constructive
interference occurs

$$n\lambda = MP + PN \qquad n = 1, 2, 3\ldots.$$

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

19
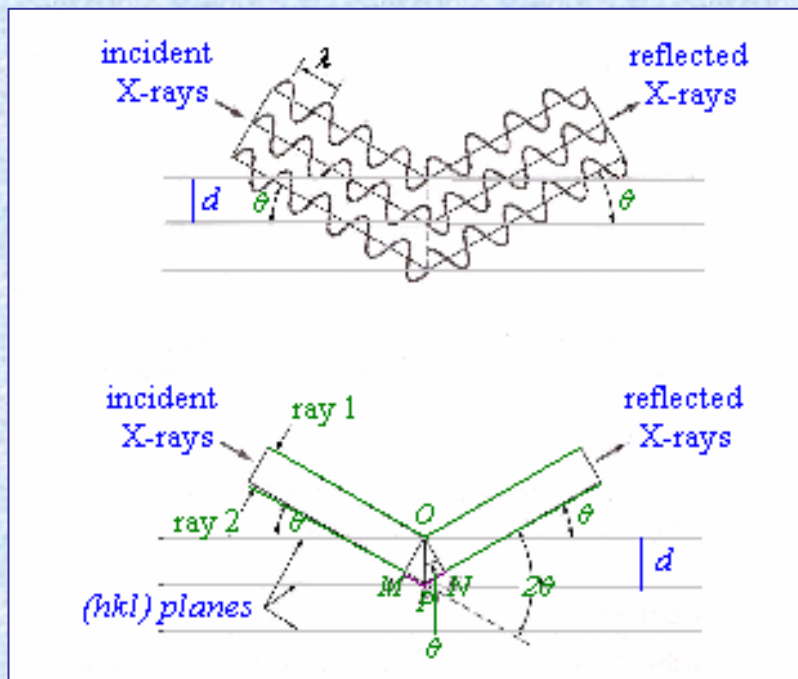
ex. BCC Fe placed in an x-ray diffractometer using x-ray with $\lambda = 0.1541$ nm. diffraction from {110} planes was obtained at $2\theta = 44.704°$. calculate lattice constant a.

$$\lambda = 2\, d_{110}\, \sin\theta$$

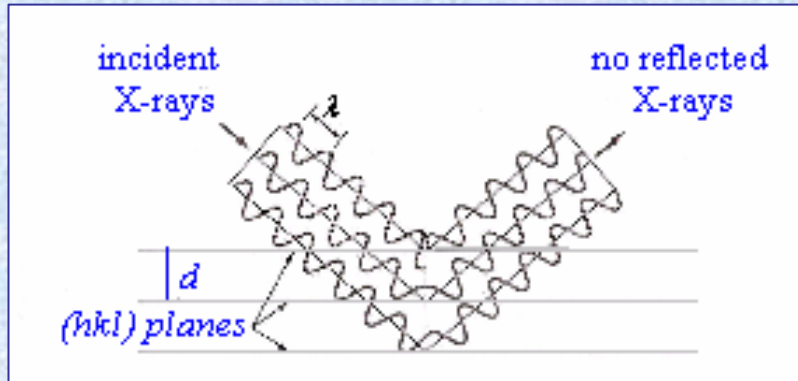$$d_{110} = \frac{\lambda}{2\sin\theta} = \frac{0.1541 \text{ nm}}{2\sin(22.352°)} = 0.2026 \text{ nm}$$

$$a = d_{hkl}\sqrt{h^2 + k^2 + l^2} = 0.2026\sqrt{2} = 0.287 \text{ nm}$$

X-ray diffraction analysis of crystal structures
  powder diffraction method
  diffractometer
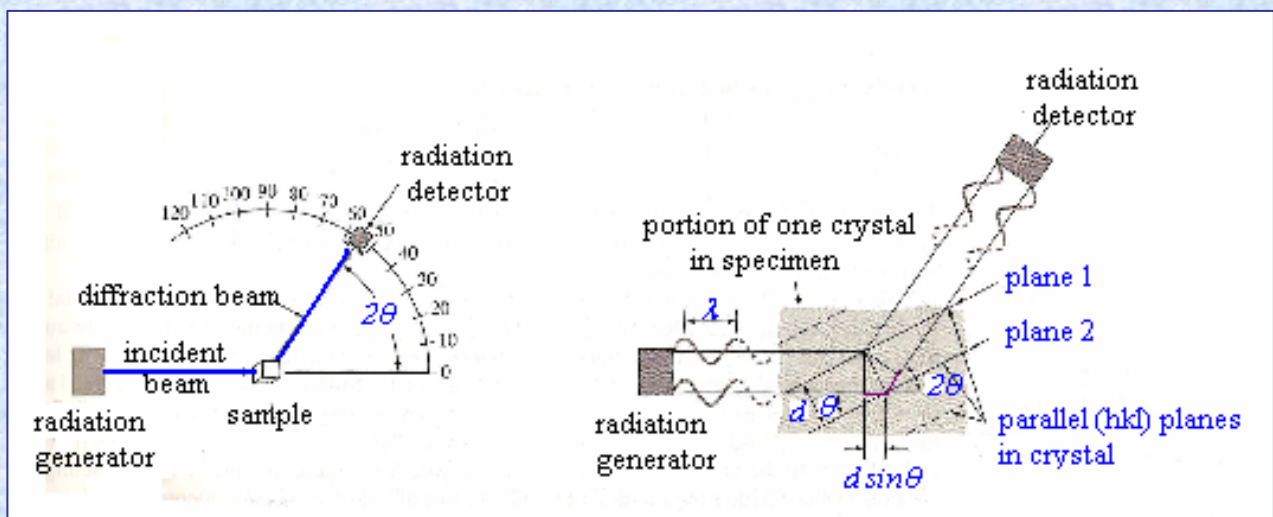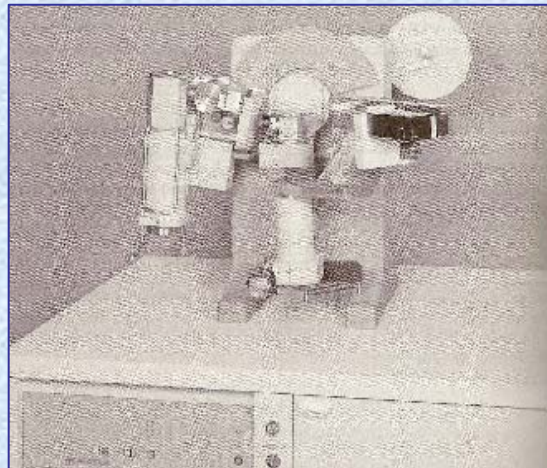
diffraction pattern for cubic unit cell

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad \text{and} \quad \lambda = 2d \sin\theta$$

$$\lambda = \frac{2a \sin\theta}{\sqrt{h^2 + k^2 + l^2}}$$

rules for determining the diffracting {*hkl*} planes in cubic crystals

	reflection present	reflection 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

ex. Diffraction pattern for W sample by the use of a diffractometer with Cu radiation
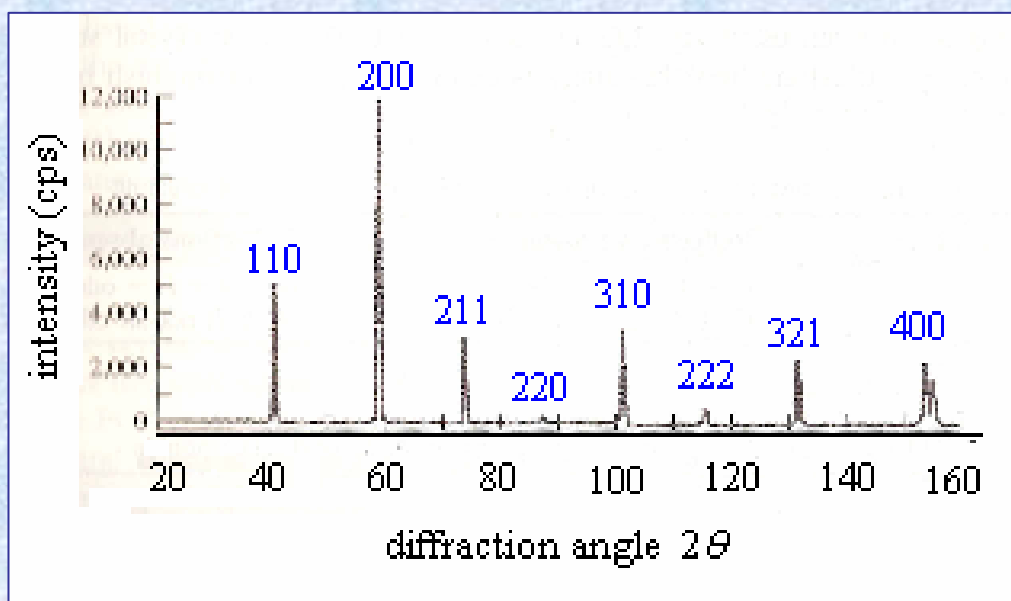
W : BCC structure

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

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

$$\frac{\sin^2\theta_A}{\sin^2\theta_B} = \frac{h^2{}_A + k^2{}_A + l^2{}_A}{h^2{}_B + k^2{}_B + l^2{}_B}$$

Miller indices of the diffracting planes for BCC and FCC

{hkl}	$\Sigma[h^2 + k^2 + l^2]$	FCC	BCC
{100}	1	…..	…..
{110}	2	…..	110
{111}	3	111	…..
{200}	4	200	200
{210}	5	…..	…..
{211}	6	…..	211

first two sets of diffraction planes
FCC   {111) and {200}

$$\frac{\sin^2\theta_A}{\sin^2\theta_B} = \frac{h^2{}_A + k^2{}_A + l^2{}_A}{h^2{}_B + k^2{}_B + l^2{}_B} = 0.75$$

BCC {110) and {200}

$$\frac{\sin^2\theta_A}{\sin^2\theta_B} = \frac{h^2_A + k^2_A + l^2_A}{h^2_B + k^2_B + l^2_B} = 0.5$$

ex. an element that has either BCC or FCC structure shows diffraction peaks at following 2θ angles: 40, 58, 73, 86.8, 100.4 and 114.7. wavelength of x-ray $\lambda = 0.154$

a. BCC or FCC?

b. determine the lattice constant a.

c. identify the element.

(a)

2θ	θ	$\sin\theta$	$\sin^2\theta$
40	20	0.3420	0.1170
58	29	0.4848	0.2350
73	36.5	0.5948	0.3538
86.8	43.4	0.6871	0.4721
100.4	50.2	0.7683	0.5903

first and second angles

0.1170/0.3420 = 0.5   BCC structure

(b) $$a = \frac{\lambda}{2}\frac{\sqrt{h^2+k^2+l^2}}{\sin\theta} = \frac{0.154}{2}\frac{\sqrt{2}}{0.342}$$

$= 0.318$ nm

(c) W