Crystalline Solid Structure

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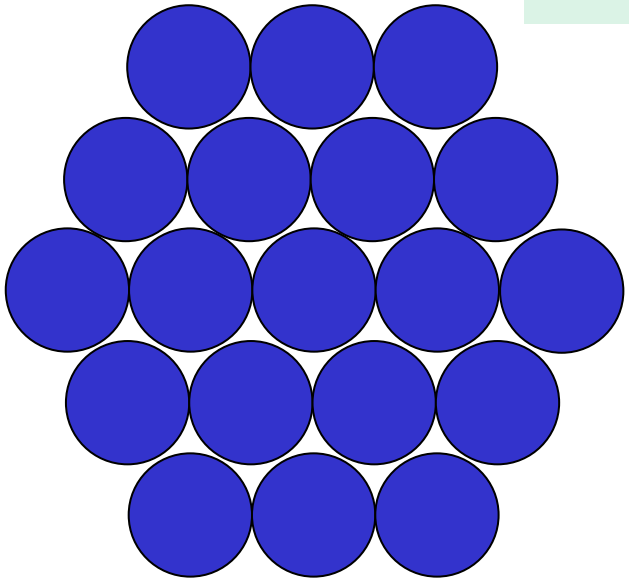
Objectives

- 면심입방 (Face-Centered Cubic), 체심입방 (Body-Centered Cubc), 육방조밀 (Hexagonal Close-Packed) 격자 구조 이해
- FCC와 BCC에서 Unit cell의 lattice parameter와 Hardsphere 원자 모형을 사용하여 원자 반지름을 구할 수 있다.
- 주어진 Unit cell에서 FCC와 BCC의 금속 밀도 계산
- 원자 조밀 충진면(close-packed plane)의 적층(stacking)에 의해 FCC, HCP가 생기는 과정 설명
- X선 회절 현상과 결정학

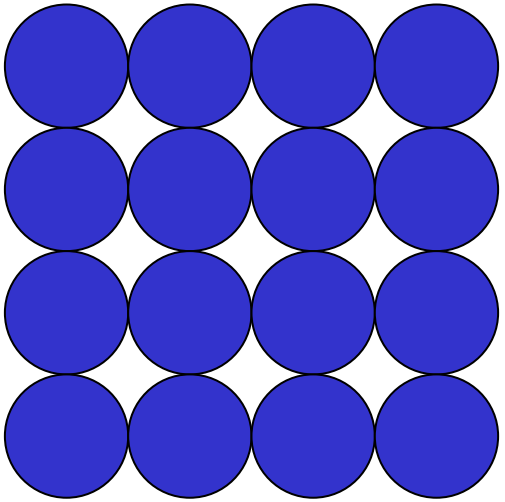
Metallic Crystal Structures

- How can we stack (hard-sphere) metal atoms to minimize empty space?

2-dimension



vs.

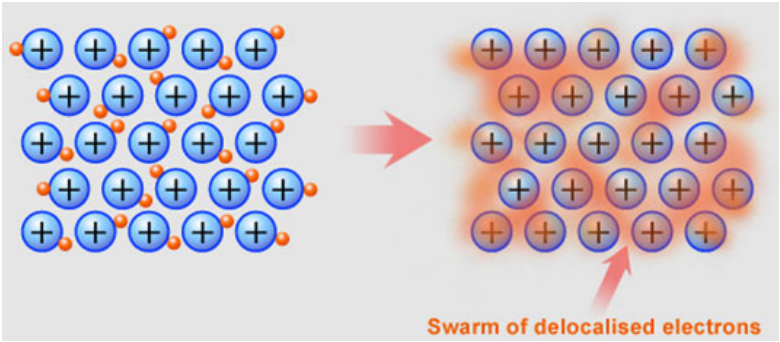


Now, how can we stack these 2-D layers to

make 3-D structures while minimizing the empty space?

Metallic Crystal Structures

- 금속 재료는 금속결합을 하며, 결합의 방향성이 없어 최인접 원자의 개수나 위치에 대한 제약이 없다. 따라서 최인접 원자가 많이 존재하고, 조밀한 원자 충진(packing)을 갖는다.
- 대부분 금속 원자는 FCC, BCC, HCP 구조를 가진다.



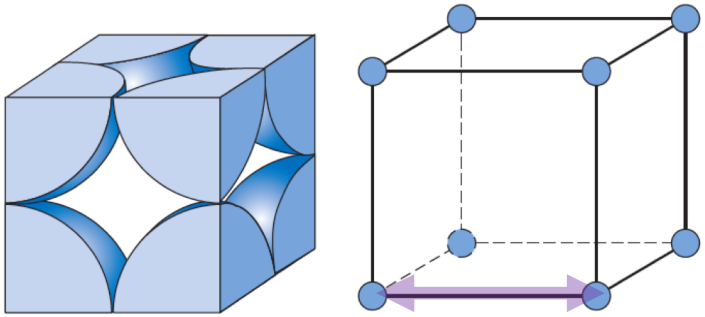
- Simple Cubic
- Face-centered cubic
- Body-centered cubic
- Hexagonal close-packed

언급된 결정 구조에서 다음의
두 항목을 먼저 익히자

- Atomic packing factor (APF; 원자 충진율)
- Close-packed direction (if any)

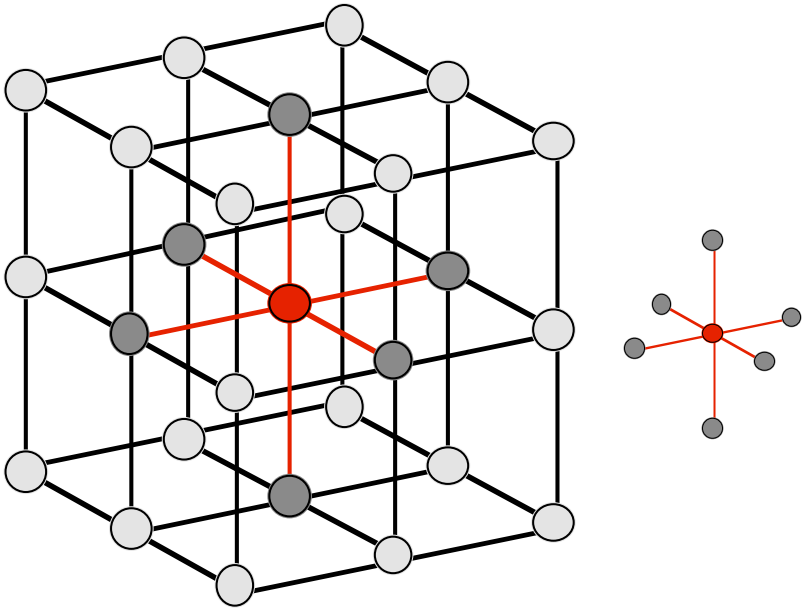
Simple Cubic Structure (SC)

- Rare due to low packing density; only Po(폴로늄) has this structure.



- Close-packed directions are cube edges.

- Coordination # (배위수) = 6
(# of nearest neighbors; 최근접 원자 수)



- Lattice parameter a, radius of the atom R: a=2R
- The number of atom in the unit cell? 1
- Why? An atom in the corner is 'shared' by 8 neighboring unit cell.

- 원자 충진율 (얼마나 조밀한 결정 구조인지): Atomic packing factor (APF) – 다음 slide

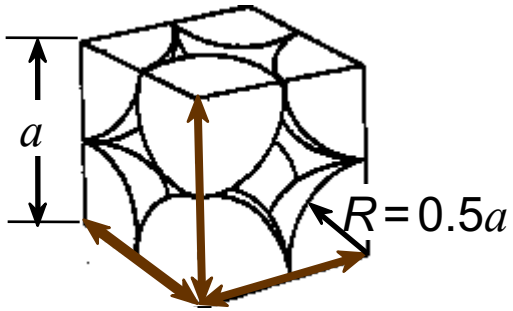
Fig. 4.2, *Callister & Rethwisch 9e.*

Atomic Packing Factor (APF)

$$APF = \frac{\text{Volume of (hard-sphere) atoms in unit cell*}}{\text{Volume of unit cell}}$$

*assume hard spheres

- APF for a simple cubic structure = 0.52



close-packed directions

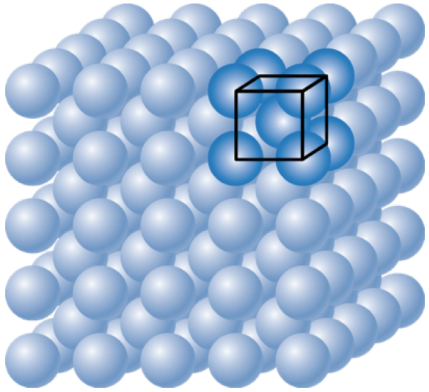
contains 8 x 1/8 =
1 atom/unit cell

$$APF = \frac{\text{atoms}}{\text{unit cell}} \cdot \frac{\text{volume}}{\text{atom}} \Big/ \frac{\text{volume}}{\text{unit cell}}$$

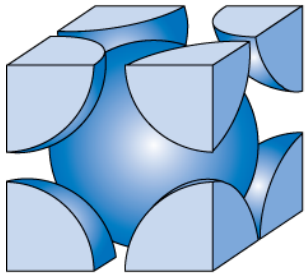
$$APF = \frac{1 \cdot \frac{4}{3}\pi(0.5a)^3}{a^3}$$

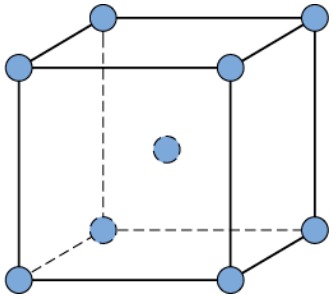
Adapted from Fig. 4.2 (a), *Callister & Rethwisch 9e.*

Body-Centered Cubic Structure (BCC)



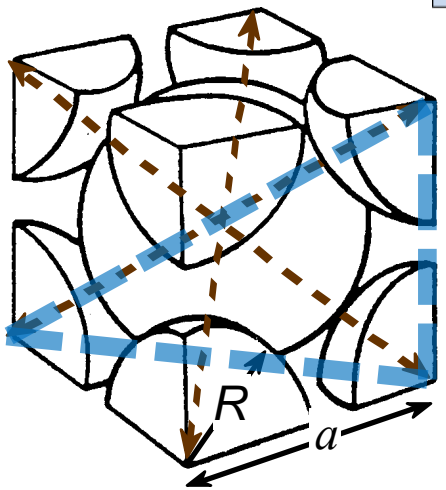
- Atoms touch each other along cube diagonals.
- ex: Cr, W, Fe (α), Tantalum, Molybdenum



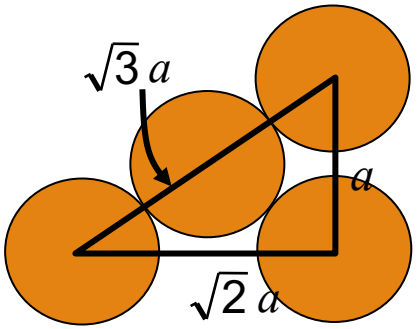


- Coordination # = 8

- 2 atoms/unit cell:
  1 center + 8 corners x 1/8



Close-packed direction
(cube diagonal)



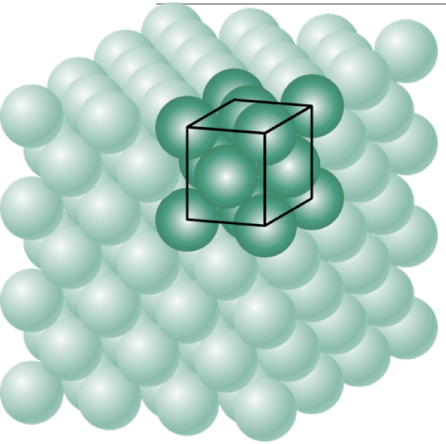
Close-packed directions:
length = $4R = \sqrt{3}\,a$

$$\text{APF} = \frac{\dfrac{\text{atoms}}{\text{unit cell}} \cdot \dfrac{\text{volume}}{\text{atom}}}{\dfrac{\text{volume}}{\text{unit cell}}} = \frac{2\left(\frac{4}{3}\pi\left(\frac{\sqrt{3}a}{4}\right)^3\right)}{a^3}$$

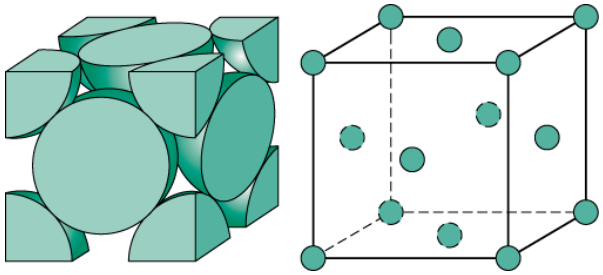
- APF for a body-centered cubic structure = 0.68

Adapted from Fig. 4.1,
Callister & Rethwisch 9e.

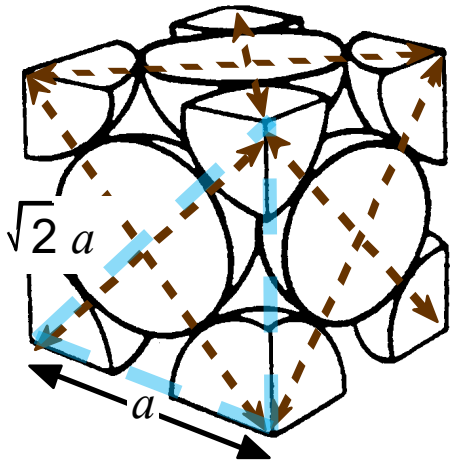
Face Centered Cubic Structure (FCC)

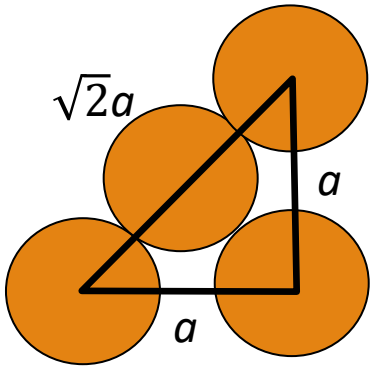


- Atoms touch each other along face diagonals.
- ex: Al, Cu, Au, Pb, Ni, Pt, Ag



- Coordination # = 12
- 4 atoms/unit cell:
  6 face x 1/2 + 8 corners x 1/8





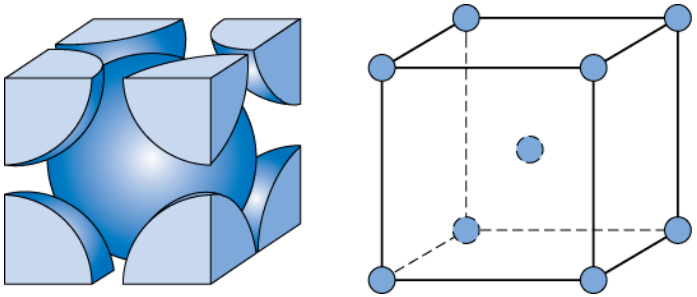
Close-packed directions:
length = $4R = \sqrt{2}\,a$

$$\text{APF} = \frac{\dfrac{\text{atoms}}{\text{unit cell}} \cdot \dfrac{\text{volume}}{\text{atom}}}{\dfrac{\text{volume}}{\text{unit cell}}} = \frac{4 \cdot \frac{4}{3}\pi\left(\frac{\sqrt{2}a}{4}\right)^3}{a^3}$$

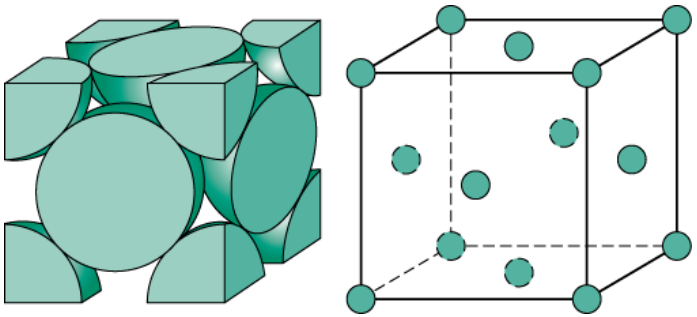
- APF for a face-centered cubic structure = 0.74

BCC, FCC 비교

- BCC
  - Coordinate #: 8
  - # of atoms per unit cell: 2
  - APF: 0.68



- FCC
  - Coordinate #: 12
  - # of atoms per unit cell: 4
  - APF: 0.74

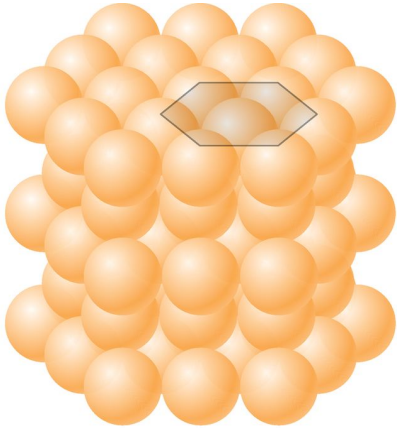


- 대부분의 단위정의 경우 원자수 계산법

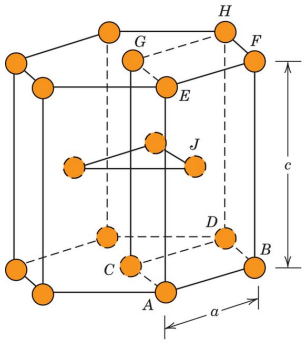
$$N = N_i + \frac{N_f}{2} + \frac{N_c}{8}$$

where N_i: # inside the unit cell; N_f on the faces; N_c: on the corners

Hexagonal Close-Packed Structure (HCP)



- 육각모양의 조밀 적층 (close-packed) 구조 (ABDC-EFHG를 간혹 unit cell로)
- ex: Cd, Mg, Ti, Zn

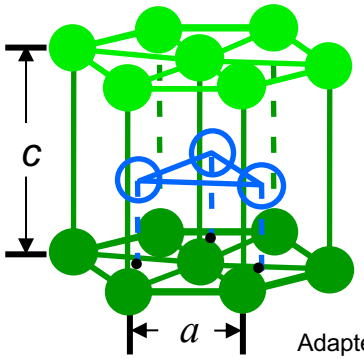


- Coordination # = 12
- 6 atoms/unit cell

$$= 3\times1(inside) + 12\times\frac{1}{6}(corners) + 2\times\frac{1}{2}(basal\ plane)$$

- APF = 0.74 (same as that of FCC) – see Ex. 4.3
- c/a = 1.633

- 3D Projection



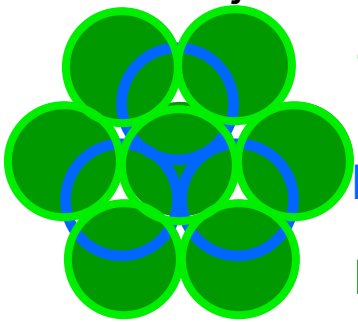
A sites

B sites

A sites

Adapted from Fig. 4.3(a), *Callister & Rethwisch 9e.*

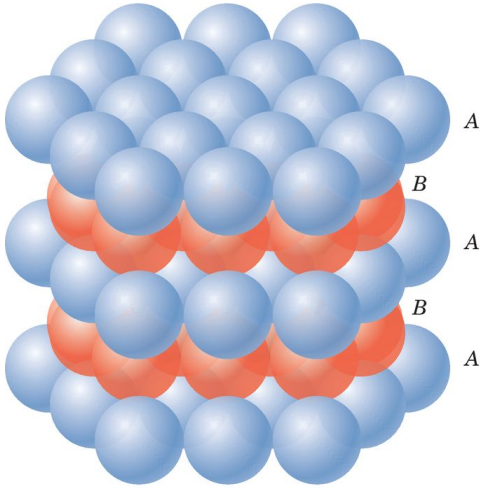
- 2D Projection



Top layer

Middle layer

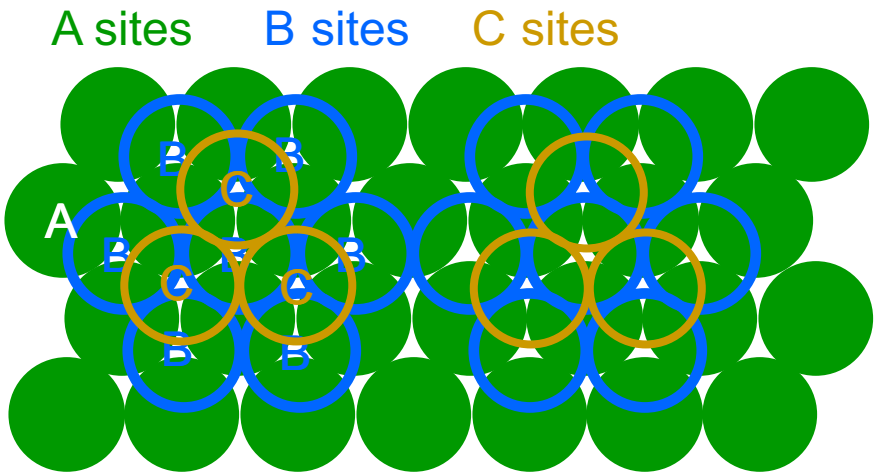
Bottom layer



Adapted from W. G. Moffatt, G. W. Pearsall, and J. Wulff, The Structure and Properties of Materials, Vol. I, Structure, p. 51. Copyright © 1964 by John Wiley & Sons, New York.

FCC Stacking Sequence (Fig 4.23a)

- ABCABC... Stacking Sequence
- 2D Projection



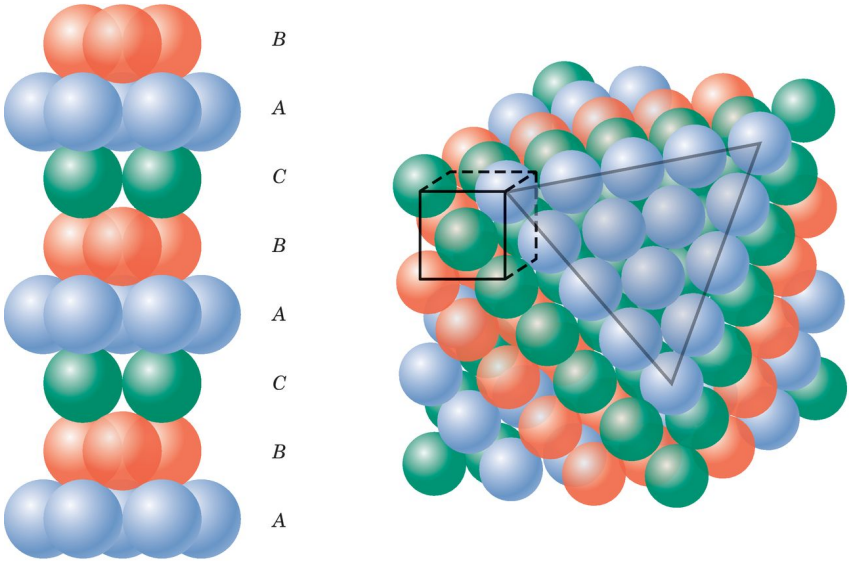
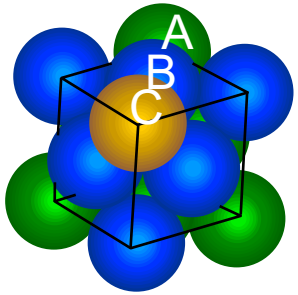


Figure (b) from W. G. Moffatt, G. W. Pearsall, and J. Wulff, The Structure and Properties of Materials, Vol. I, Structure, p. 51. Copyright © 1964 by John Wiley & Sons, New York.

- FCC Unit Cell



Theoretical Density, ρ

- **Using the crystallographic structure**, the density can be 'theoretically' calculated.

$$\text{Density} = \rho = \frac{\text{mass}}{\text{unit volume}}$$

$$= \frac{\text{mass per unit cell}}{\text{volume of unit cell}}$$

$$= \frac{\text{\# of Atoms per unit cell} \times \text{mass of an atom}}{\text{Vol. per unit cell}}$$

$$= \frac{\text{\# of atoms per unit cell} \times \text{mass of an atom} \times \text{Avog. \#}}{\text{Vol. per unit cell} \times \text{Avog. \#}}$$

$$\rho = \frac{n A}{V_C N_A} \qquad \text{Eq 4.8}$$

where

n = number of atoms/unit cell

A = atomic weight

V_C = Volume of unit cell = a^3 for cubic

N_A = Avogadro's number

= 6.022×10^{23} atoms/mol

Theoretical Density, ρ

- Ex: Cr (BCC)

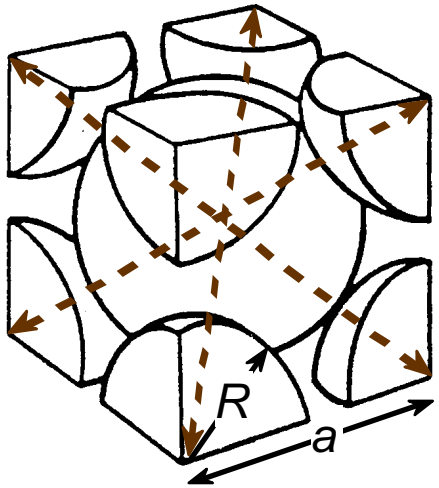
A (Atomic weight) = 52.00 g/mol

R (Atom radius) = 0.125 nm

n (# of atoms in unit cell) = 2 atoms/unit cell

Relationship between lattice parameter (a) and radius:

$$a = \frac{4R}{\sqrt{3}} = 0.2887\ nm$$



Adapted from Fig. 4.1(a), *Callister & Rethwisch 9e.*

$$\rho = \frac{n\,A}{V_C N_A}$$

$$\rho = \frac{\dfrac{\text{atoms}}{\text{unit cell}} \times \dfrac{\text{g}}{\text{mol}}}{\text{volume} \times \dfrac{\text{atoms}}{\text{mol}}}$$

$$\rho = \frac{2 \times 52.00}{a^3 \times 6.022 \times 10^{23}}$$

volume / unit cell

atoms / mol

$\rho_{theoretical}$	= 7.18 g/cm^3
ρ_{actual}	= 7.19 g/cm^3

Densities of Material Classes

In general

$\rho_{metals} > \rho_{ceramics} > \rho_{polymers}$

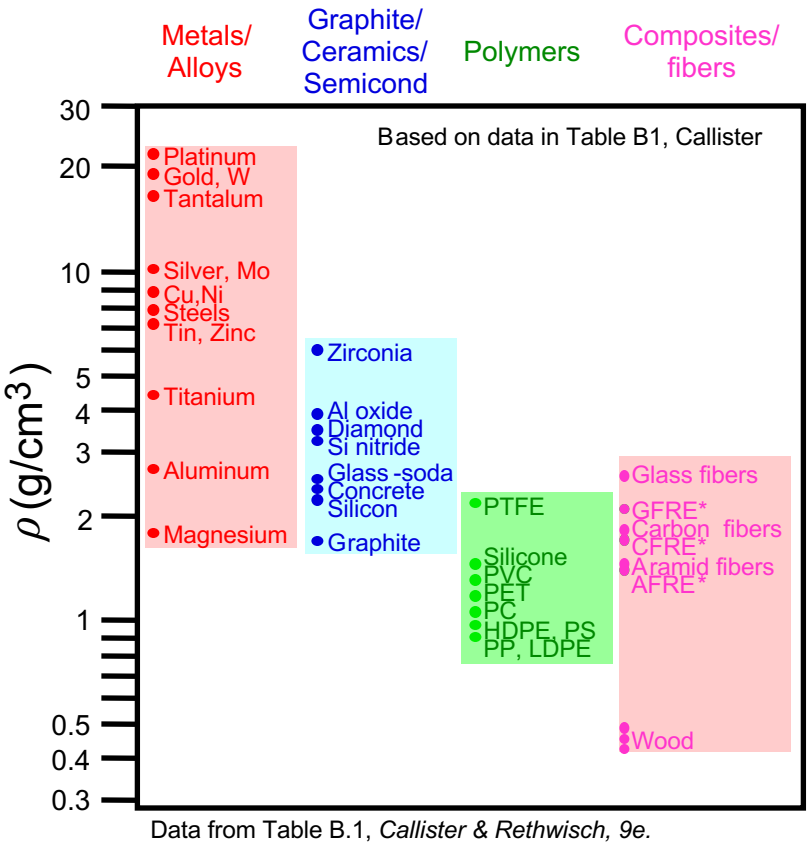
Why?

Metals have...
- close-packing (metallic bonding)
- often large atomic masses

Ceramics have...
- less dense packing
- often lighter elements

Polymers have...
- low packing density (often amorphous)
- lighter elements (C,H,O)

Composites have...
- intermediate values



Data from Table B.1, *Callister & Rethwisch, 9e.*

Polymorphism

- 한 금속 원소가 하나 이상의 결정 구조를 가질 수 있을 때.
- 같은 금속 원소지만 다른 결정 구조를 가질 수 있는 현상을 “동질이상” (polymorphism)이라 한다.
- 단일 고체에서 이러한 현상을 동소체 (allotropy)라 함.
- 결정 구조의 압력, 온도 의존성.
- 탄소/다이아몬드
- 철 – BCC (대부분의 철, 강) or FCC (대부분의 스테인레스 강) or even HCP
- Ti- alpha/beta

Polymorphic Forms of Carbon

Diamond

- Tetrahedral bonding of carbon
  - hardest material known
  - very high thermal conductivity
- large single crystals – gem stones
- small crystals – used to grind/cut other materials
- diamond thin films
  - hard surface coatings – used for cutting tools, medical devices, etc.

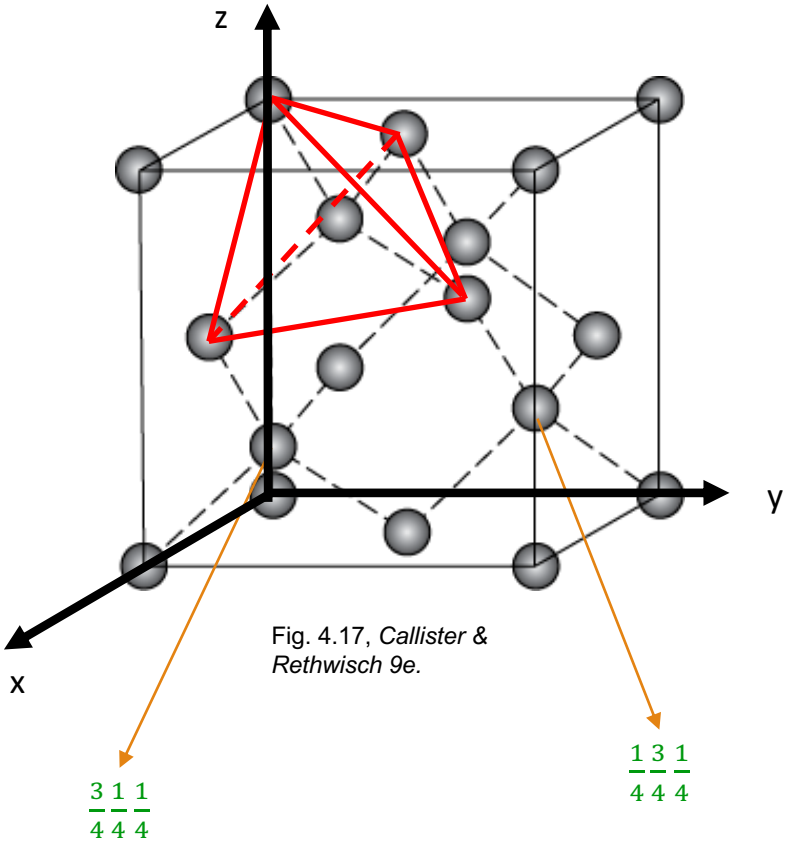
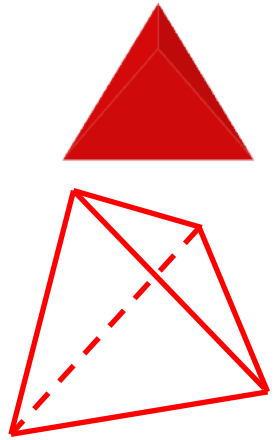


Fig. 4.17, *Callister & Rethwisch 9e.*

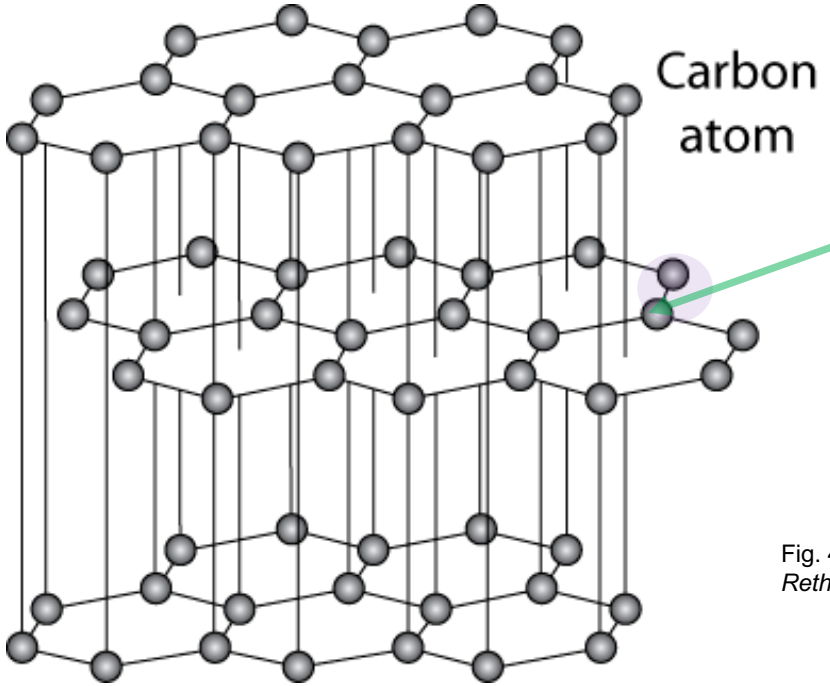


tetrahedral

Polymorphic Forms of Carbon

Graphite

- layered structure – parallel hexagonal arrays of carbon atoms



sp^2 hybrid orbital (공유 결합)

Graphene; 흑연을 점착 테이프를 이용하여 박리 (2010 노벨 물리학상)

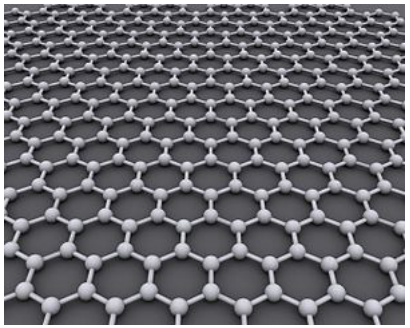
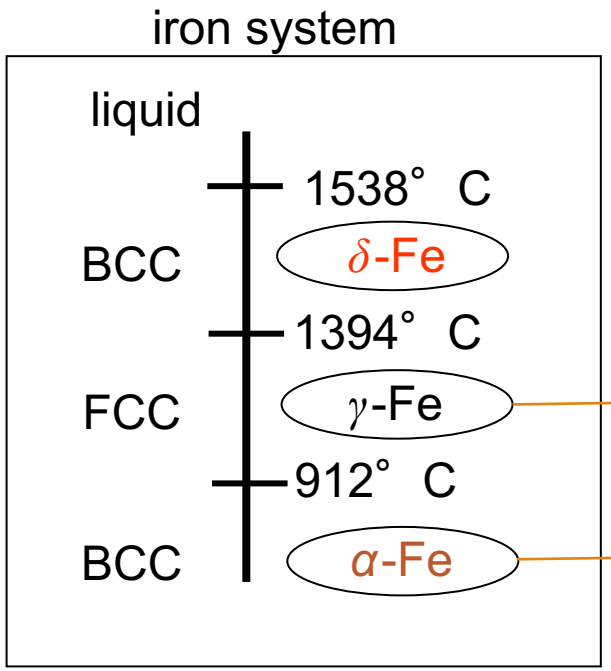


Fig. 4.18, *Callister & Rethwisch 9e.*

- weak van der Waal's forces between layers
- planes slide easily over one another -- good (solid) lubricant

Polymorphism of iron

- Two or more distinct crystal structures for the same material (allotropy/polymorphism)



Paramagnetic — 300 계열 스테인리스강

Ferromagnetism — 탄소강철 (steel)

합금 상태로 생산 – Materials Design

싱크대의 스테인레스강: 변형이 생기면 γ 상에서 $\alpha`$ 상으로 변이한다. 따라서 자석에 붙는 성질도 바뀐다.

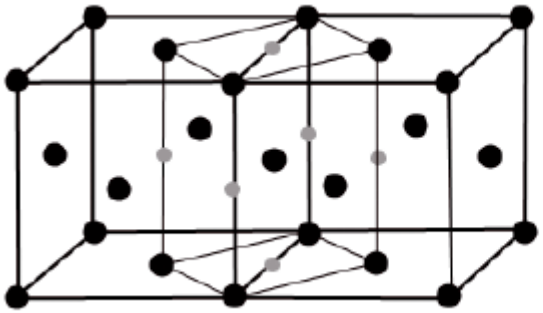
Polymorphism of iron: phase transformation

γ-Fe → α-Fe

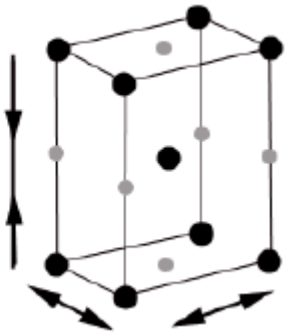
FCC BCC

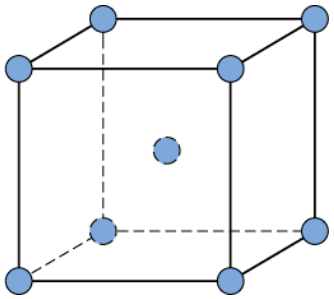
온도에 따라 에너지적으로 안정된 결정구조가 달라진다.

BCT embedded in two neighboring FCC



Distorting BCT in a certain way can result in BCC

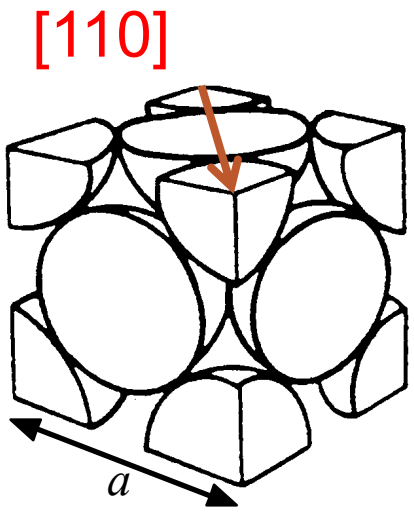




고체 상태의 FCC와 BCT의 유사성

Linear Density

- Linear Density of Atoms ≡ LD = $\dfrac{\text{Number of atoms}}{\text{Unit length of direction vector}}$



ex: linear density of Al in [110] direction
a = 0.405 nm

atoms → 2

length → $\sqrt{2}a$

$$LD = \frac{2}{\sqrt{2}a} = 3.5\ \text{nm}^{-1}$$

Adapted from Fig. 3.1(a), *Callister & Rethwisch 9e.*

Planar Density of (100) Iron

What is PD of Iron's (100) at room temperature?

At T < 912°C, iron (Fe) has the BCC structure.

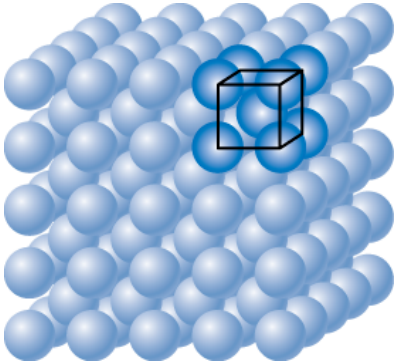
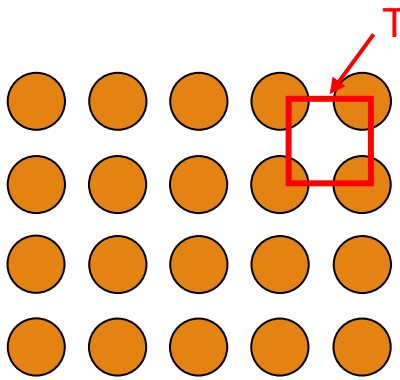


Fig. 4.2(c), *Callister & Rethwisch 9e* [from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. I, *Structure*, p. 51. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.]

(100)



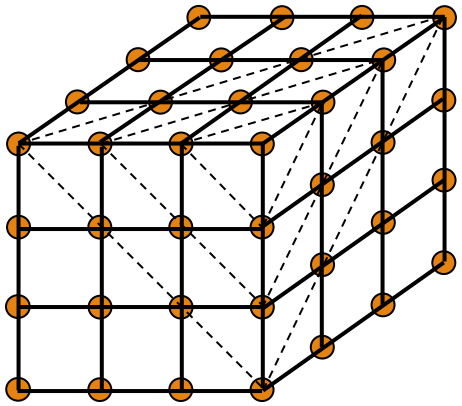
The relationship was derived from the closed-packed direction of BCC

Radius of iron R = 0.1241 nm

$$\text{Planar Density} = \frac{\text{\# of Atoms having their centers lying on the plane}}{\text{Repeated unit in 2D}} = \frac{\text{Area of atoms within the repeated unit}}{\text{Repeated unit in 2D}} = \frac{1}{a^2} = \frac{1}{\left(\frac{4\sqrt{3}}{3}R\right)^2} = 12.1 \frac{\text{atoms}}{\text{nm}^2} = 1.2 \times 10^{19} \frac{\text{atoms}}{\text{m}^2}$$

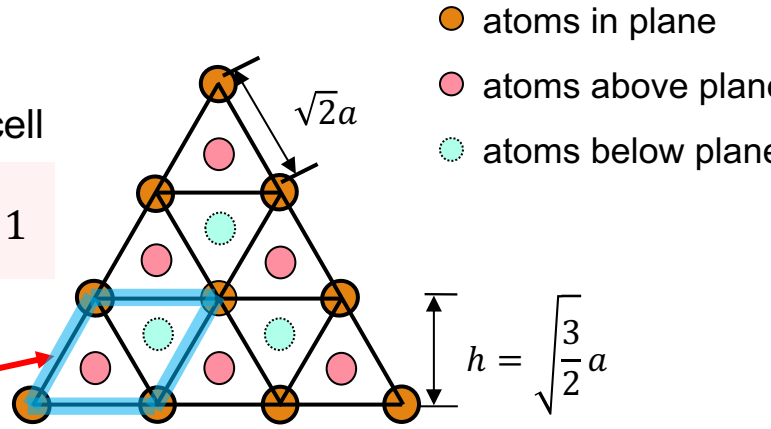
Planar Density of (111) Iron

What is PD of (111)?



1 atom in plane / unit surface cell

$$2\times\frac{60°}{360°}+2\times\frac{120°}{360°}=\frac{1}{3}+\frac{2}{3}=1$$



$$\text{area}=\sqrt{2}ah=\sqrt{3}\,a^2=\sqrt{3}\left(\frac{4\sqrt{3}}{3}R\right)^2=\frac{16\sqrt{3}}{3}R^2$$

$$\text{Planar Density}=\frac{1}{\frac{16\sqrt{3}}{3}R^2}=7.0\frac{\text{atoms}}{\text{nm}^2}=0.70\times10^{19}\frac{\text{atoms}}{\text{m}^2}$$

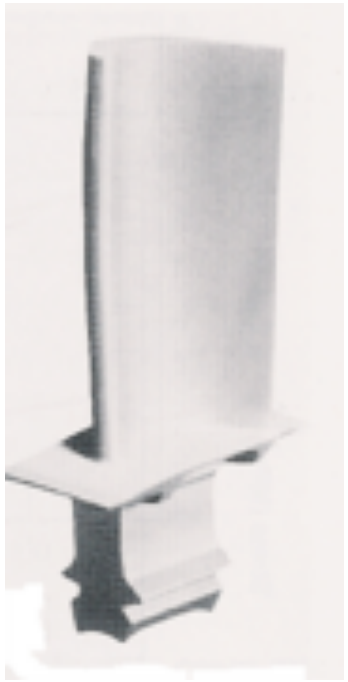
Crystals as Building Blocks

- *Some* engineering applications require single crystals:

  -- diamond single crystals for abrasives

(Courtesy Martin Deakins, GE Superabrasives, Worthington, OH. Used with permission.)

-- turbine blades



- Properties of crystalline materials often related to crystal structure.

  -- Ex: Quartz fractures more easily along some crystal planes than others.

(Courtesy P.M. Anderson)

Polycrystals

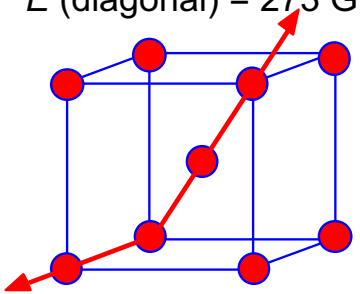
- *Most* engineering materials are polycrystals.

Fig. K, color inset pages of *Callister 5e*. (Courtesy of Paul E. Danielson, Teledyne Wah Chang Albany)

- Nb-Hf-W plate with an electron beam weld.
- Each "grain" is a single crystal.
- If grains are **randomly oriented** and **equi-axed**, overall component properties are **NOT** directional.

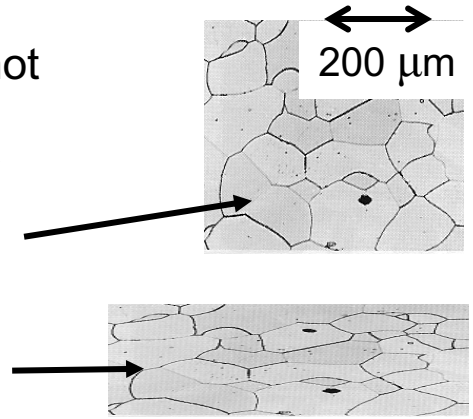
Single vs Polycrystals

- **Single Crystals**
  - -Properties vary with direction: anisotropic.
  - -Example: the modulus of elasticity (*E*) in BCC iron:



Data from Table 3.3, *Callister & Rethwisch 9e*. (Source of data is R.W. Hertzberg, *Deformation and Fracture Mechanics of Engineering Materials*, 3rd ed., John Wiley and Sons, 1989.)

- **Polycrystals**
  - -Properties may/may not vary with direction.
  - -If grains are randomly oriented: isotropic.
    ($E_{\text{poly iron}}$ = 210 GPa)
  - -If grains are textured, anisotropic.

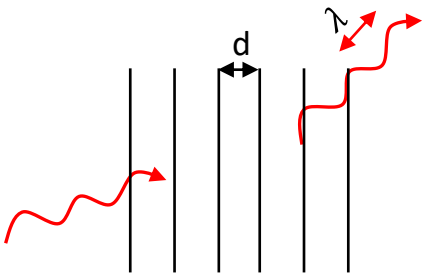


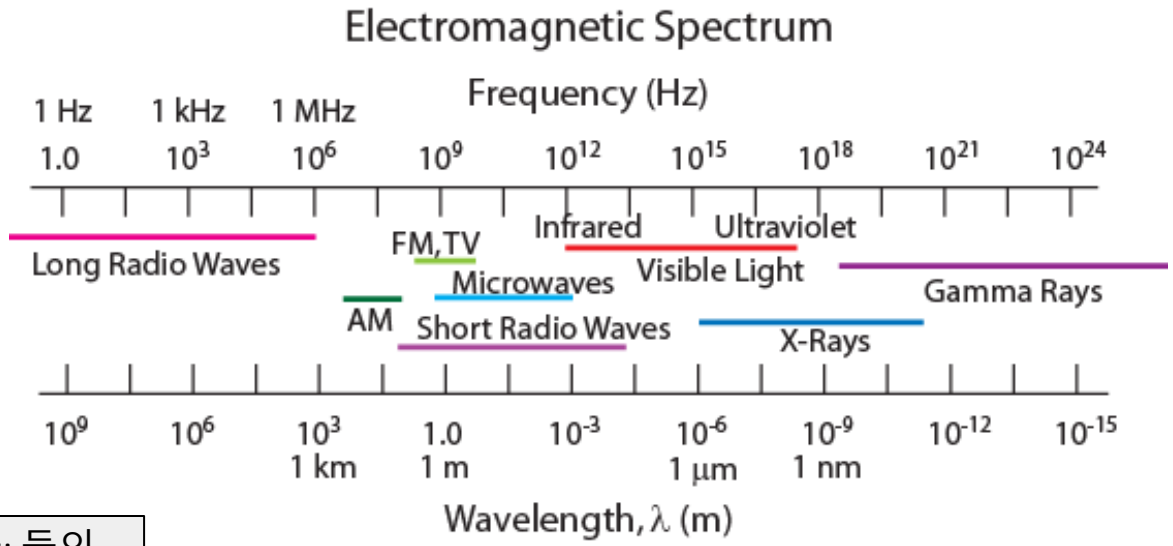
Adapted from Fig. 6.19(b), *Callister & Rethwisch 9e*. [Fig. 6.19(b) is courtesy of L.C. Smith and C. Brady, the National Bureau of Standards, Washington, DC (now the National Institute of Standards and Technology, Gaithersburg, MD).]

Texture:
- Morphological texture
- Crystallographic texture

X-Ray

X-ray: 전자기파의 한 종류





X-ray의 파장이 원자 격자 상수와 유사: 둘의 상호작용으로 인한 회절 현상 발생

- Diffraction gratings (회절 격자) must have spacings comparable to the wavelength of diffracted radiation. ($d \approx \lambda$)
- Can't resolve spacings $< \lambda$ (파장에 따라 resolution의 한계가 존재)
- For the X-ray diffraction that occurs in crystal structure, the relevant spacing is the distance between parallel planes of atoms.

Monochromatic X-ray

Monochromatic X-ray
White X-ray

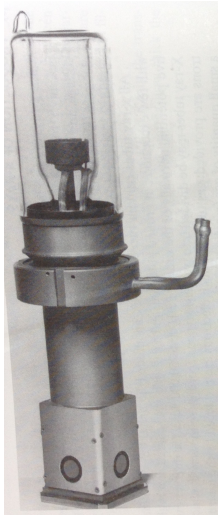
Monochromatic: 단색

빛(a type of electromagnetic waves)의 색은 그 '파장' (wavelength)로 결정된다.

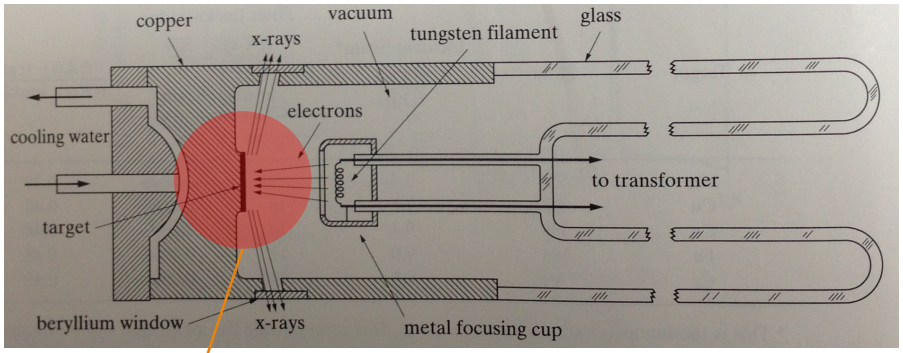
Monochromatic은 즉 단일 파장 (thus 단일 진동수)으로 이루어진 electromagnetic wave (전자기파)

(Low-power) 단색 X-ray는 원자의 전자 구조를 사용해서 만들어 낸다.
(혹은) Synchrotron 시설에서도 만들 수 있다.

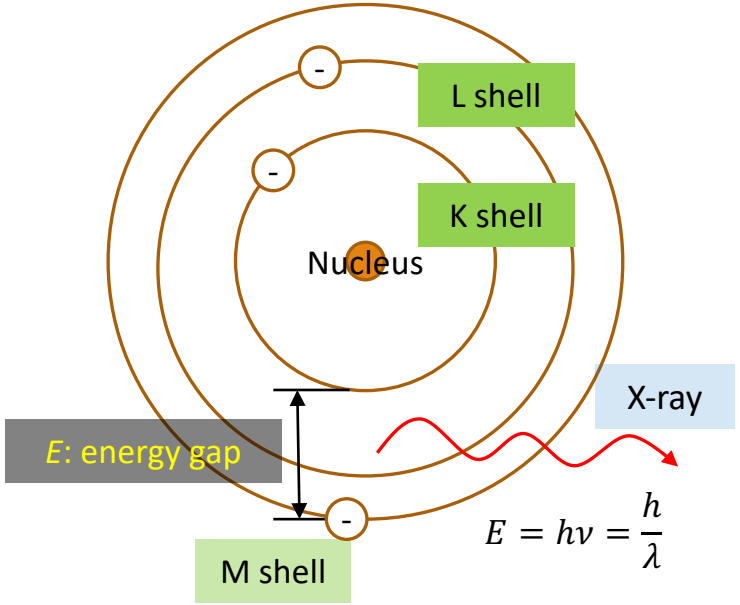
Monochromatic X-ray



X-ray tube



Target으로 쓰이는 재료마다 특정한 monochromatic X-ray (characteristic X-ray) 얻어진다.



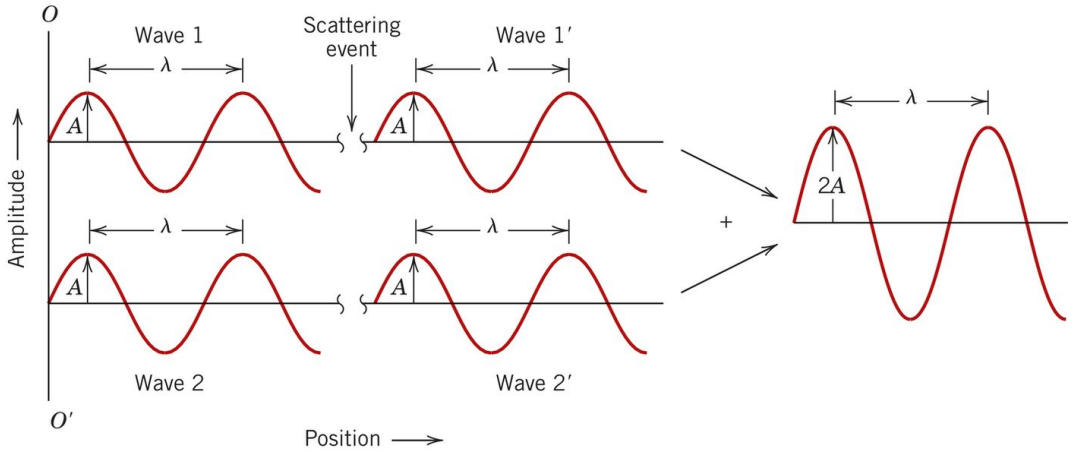
외부의 전자가 각 주 에너지각에 존재하는 전자들을 knock-off

낮은 binding energy를 가진 orbital의 전자가 inner shell의 비어진 orbital로 옮겨간다.

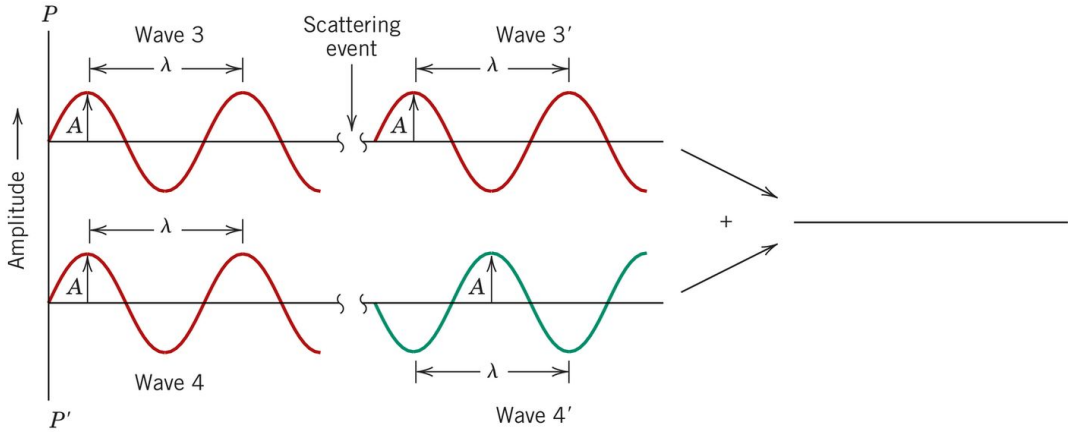
그러한 전자가 한 shell에서 다른 shell로 이동하며 EM으로 방출 (X-ray)

원자의 전자 구조는 '고유한'성질을 가지므로 단색의 X-ray 발생

X-Ray Diffraction rule



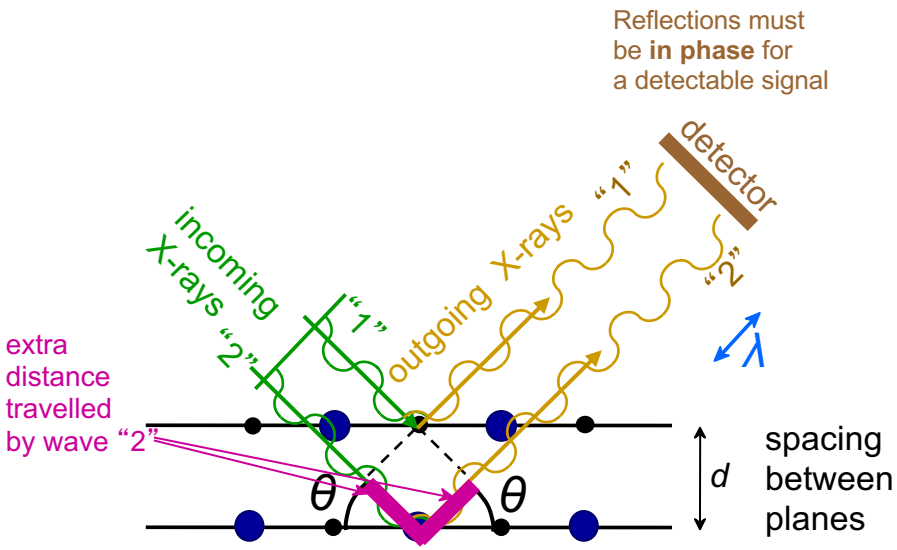
보강

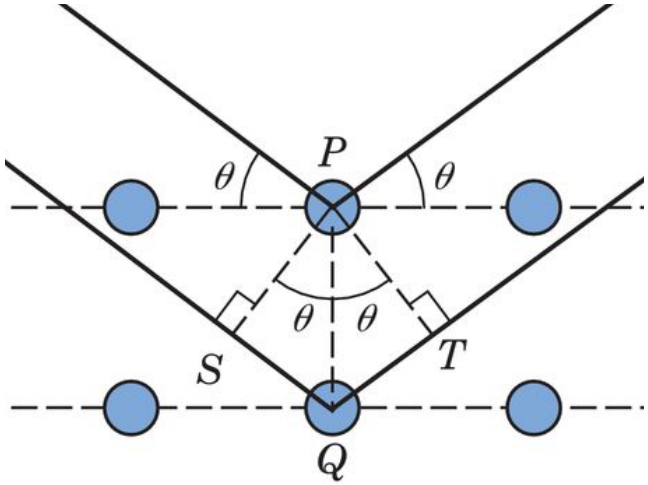


상쇄

X-Ray crystallography: X-Rays to Determine Crystal Structure

- Incoming X-rays diffract from crystal planes.

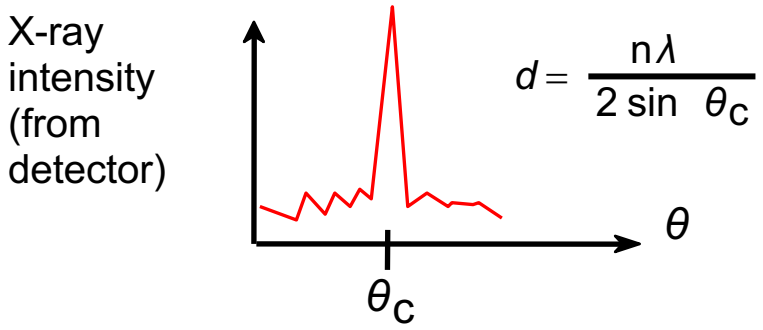




회절 조건 (Bragg's law):

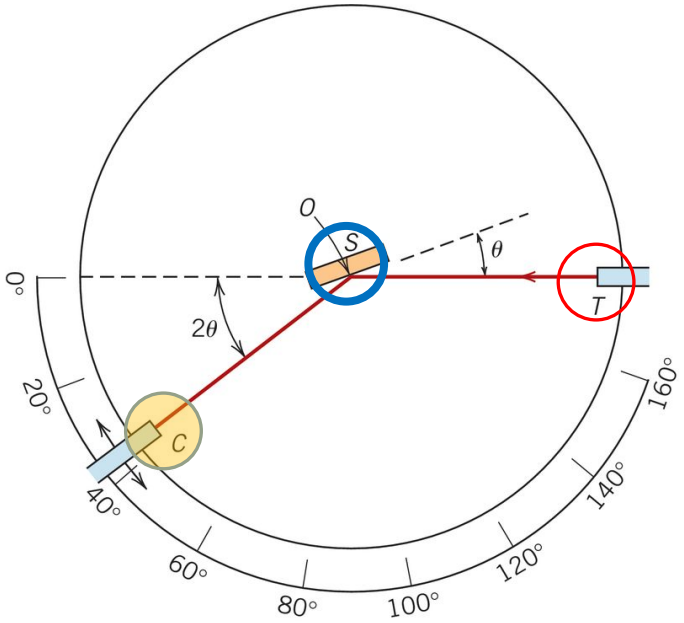
$$2 \cdot d \cdot \sin\theta = n \cdot \lambda$$

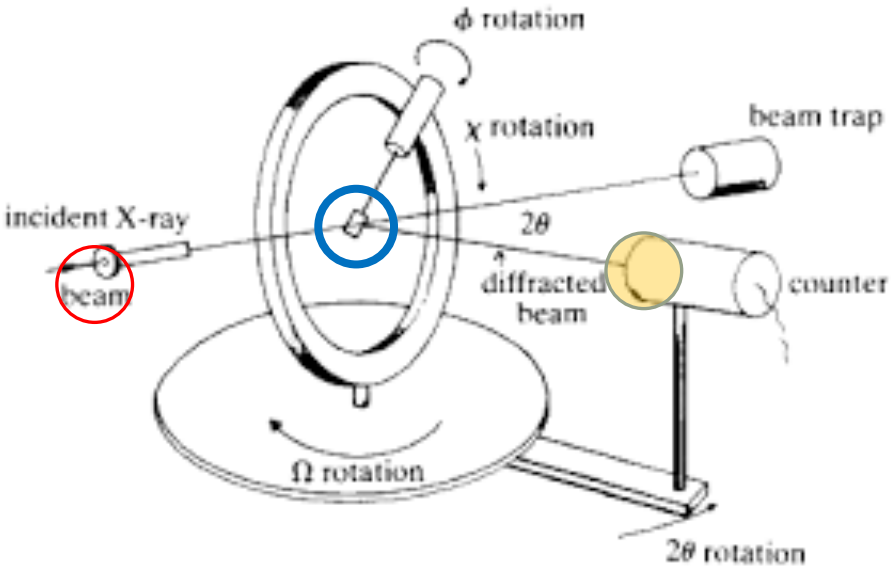
만약, X-ray target을 알고 (예를 들어 Cu), 회절 실험을 통해서 회절이 발생하는 각을 측정을 했다면, 회절이 발생한 결정면 (crystal plane)의 면간 거리(d)를 가늠할 수 있다.



Adapted from Fig. 4.29, *Callister & Rethwisch 9e*.

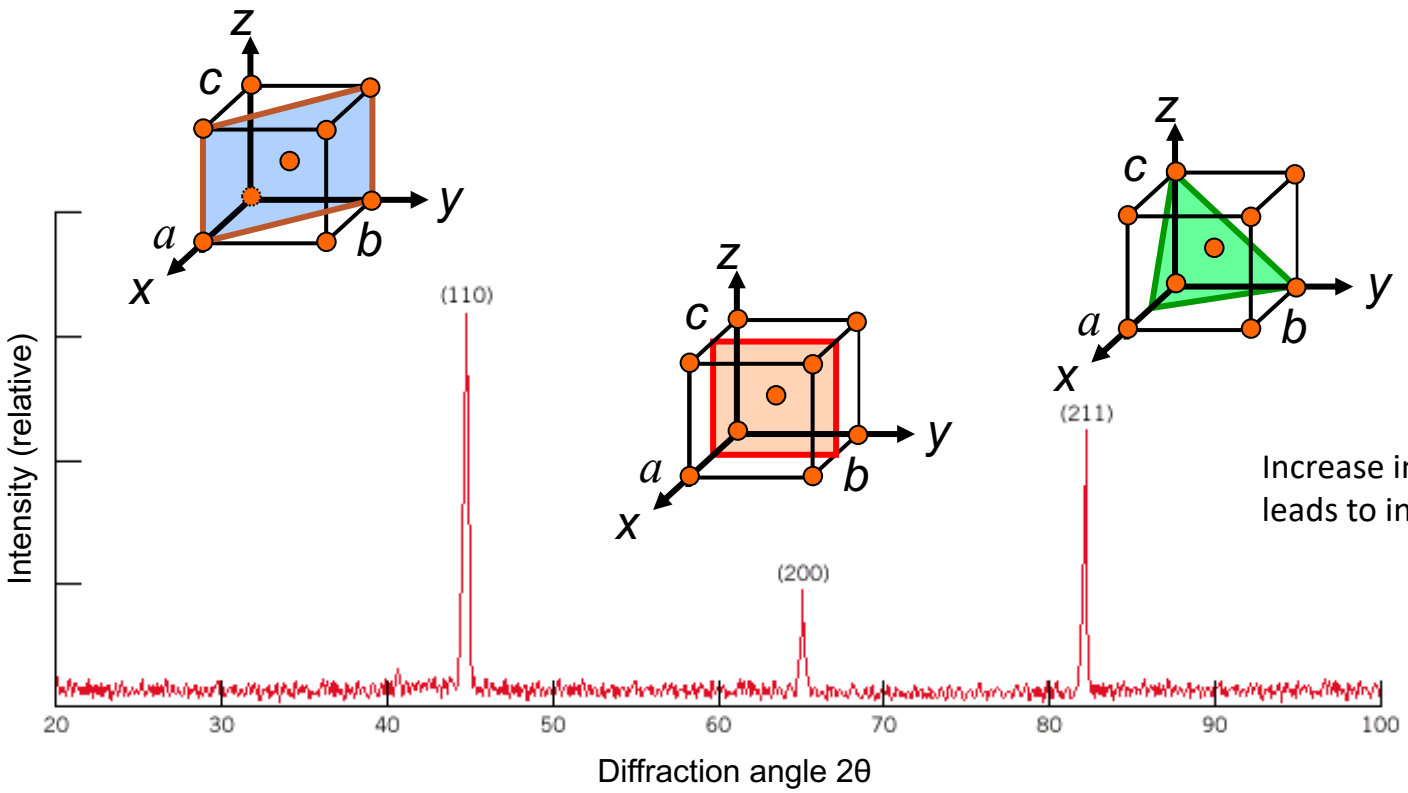
X-Ray Diffractometer - X-Ray 회절 기기





Goniometer: 한 공간에서 여러 방위로 시편을 놓기위한 장치

X-Ray Diffraction Pattern

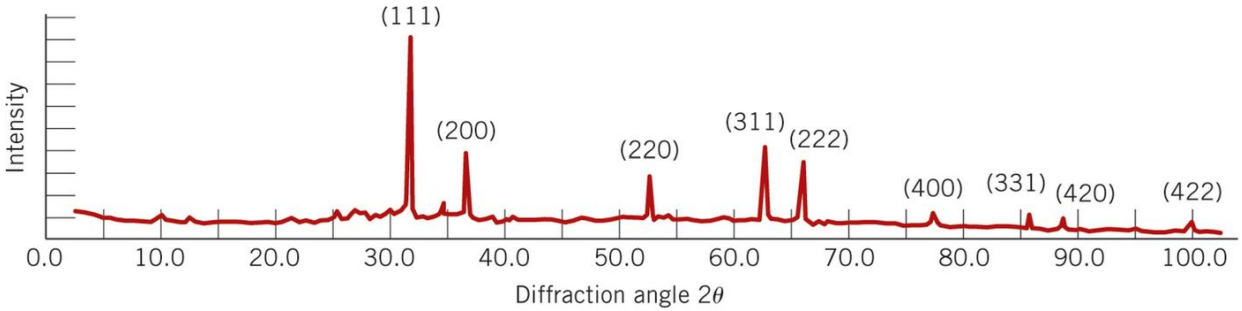


Increase in interplanar displacing leads to increase in diffraction angle.

Diffraction pattern of polycrystalline α-iron (BCC)

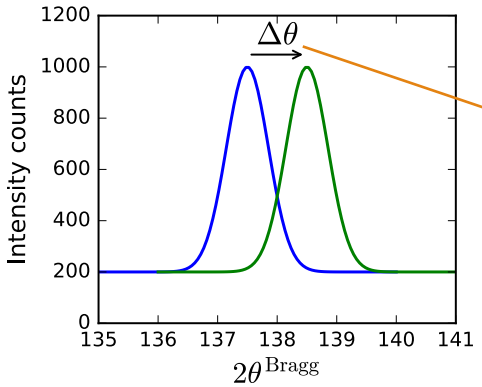
Adapted from Fig. 3.22, *Callister 8e.*

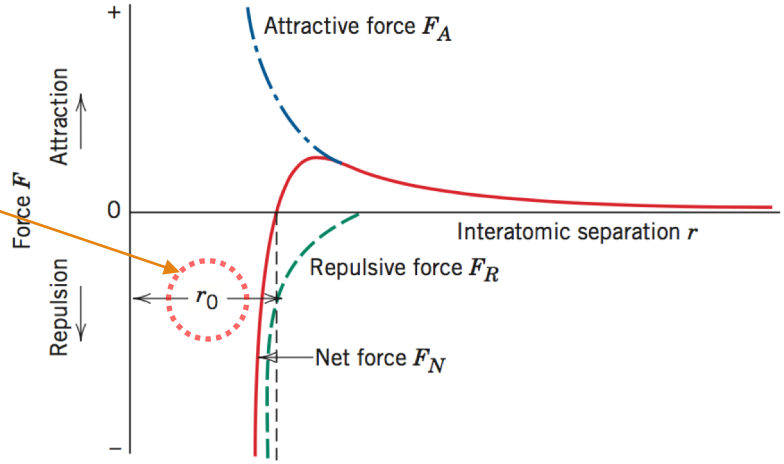
X-Ray diffraction and its applications in Materials Science



Courtesy of Wesley L. Holman.

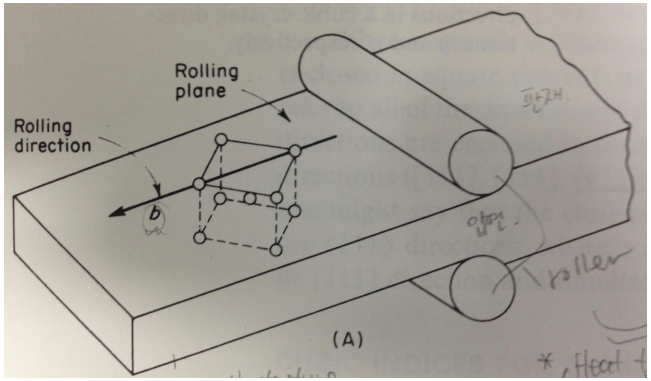
- 결정 구조를 알아낼 수 있다
- 격자 상수 (a)를 측정 가능



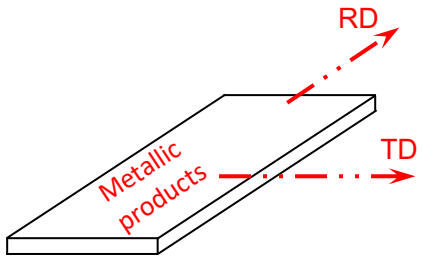


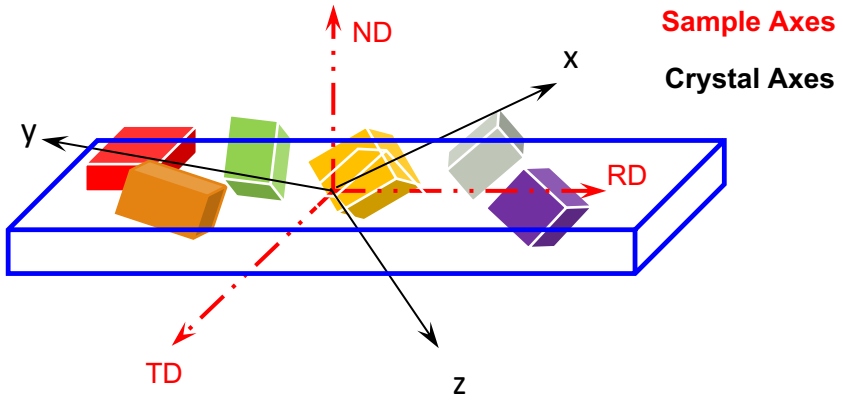
Residual stress measurement
(잔류 응력 측정)

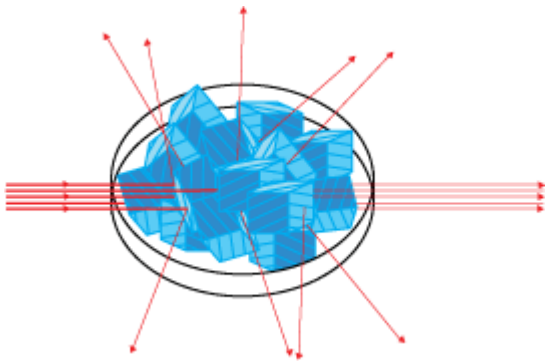
X-Ray diffraction and its applications in Materials Science



집합 조직의 측정







Polycrystal의 각 crystal 방위가 random하지 않다면 특정 방향으로 더 많이 diffraction이 발생한다.

역으로, 특정방향으로 diffraction이 강하게 발생한다면 polycrystal의 방위가 특정방향으로 많이 놓여있음을 알 수 있다. (texture가 존재)