

Crystalline Solid Structure

메카트로닉스 재료개론 (MFA9008)

창원대학교 신소재공학부

정영웅



yjeong@changwon.ac.kr
<https://youngung.github.io>
<https://github.com/youngung>

Objectives

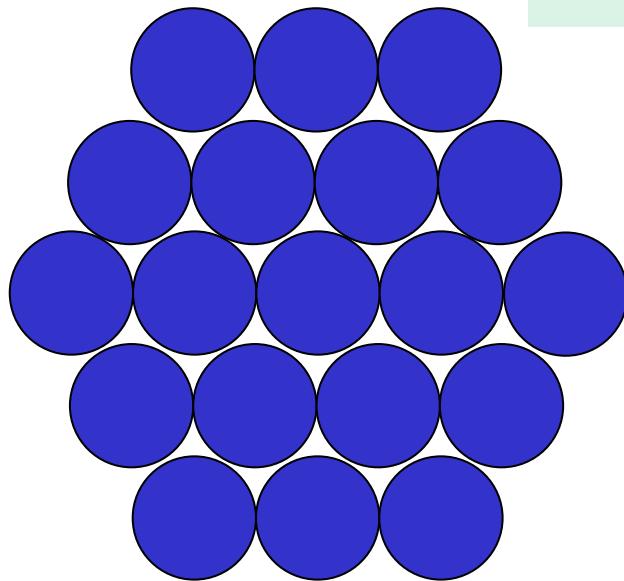
- 면심입방 (Face-Centered Cubic), 체심입방 (Body-Centered Cubc), 육방조밀 (Hexagonal Close-Packed) 격자 구조 이해
- FCC와 BCC에서 Unit cell의 lattice parameter와 Hardsphere 원자 모형을 사용하여 원자 반지름을 구할 수 있다.
- 주어진 Unit cell에서 FCC와 BCC의 금속 밀도 계산
- 원자 조밀 충진면(close-packed plane)의 적층(stacking)에 의해 FCC, HCP가 생기는 과정 설명
- X선 회절 현상과 결정학



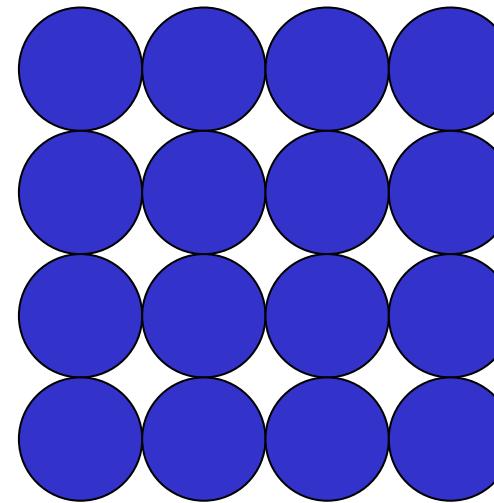
Metallic Crystal Structures

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

2-dimension



vs.

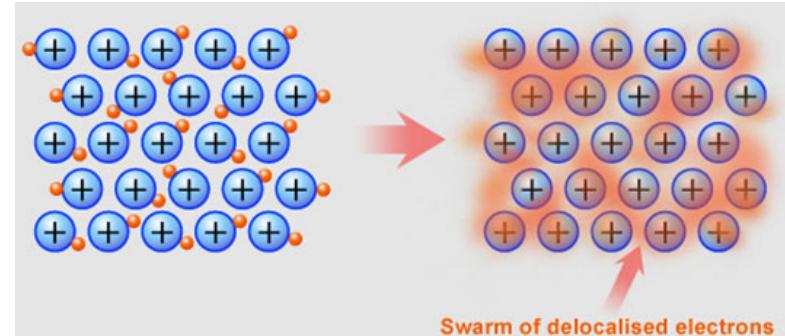


Now, how can we stack these 2-D layers to make 3-D structures while minimizing the empty space?



Metallic Crystal Structures

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

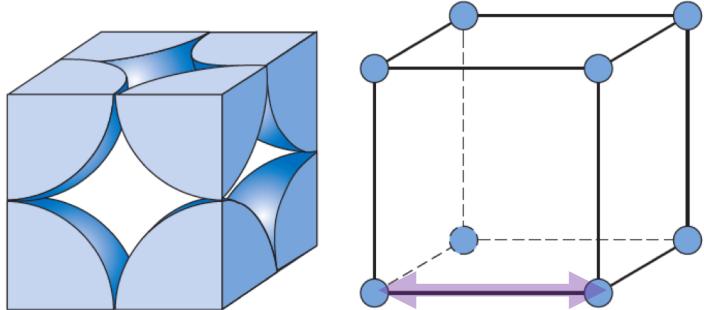


- Simple Cubic
 - Atompic packing factor (APF; 원자 충진율)
 - Close-packed direction (if any)
- Face-centered cubic
- Body-centered cubic
- Hexagonal close-packed



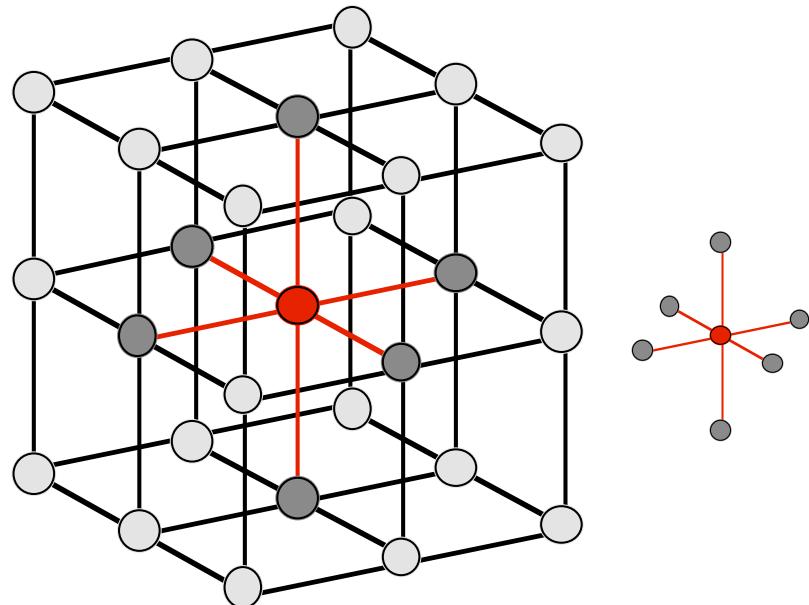
Simple Cubic Structure (SC)

- 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.

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

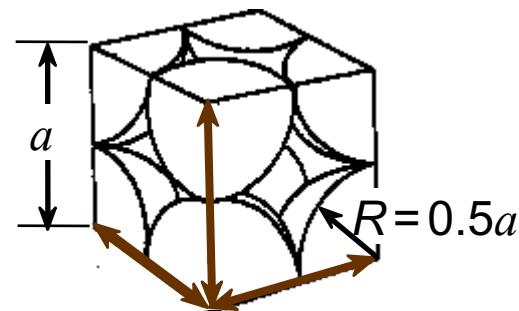


Atomic Packing Factor (APF)

$$APF = \frac{\text{Volume of atoms in unit cell}^*}{\text{Volume of unit cell}}$$

*assume hard spheres

- APF for a simple cubic structure = 0.52

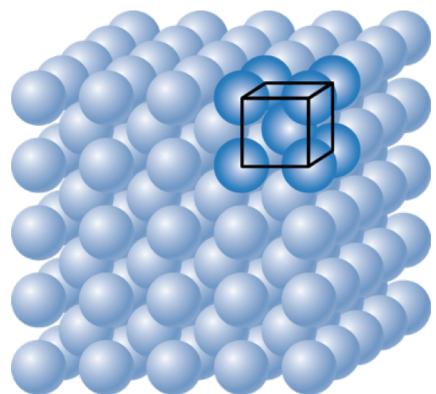


close-packed directions
contains $8 \times 1/8 =$
1 atom/unit cell

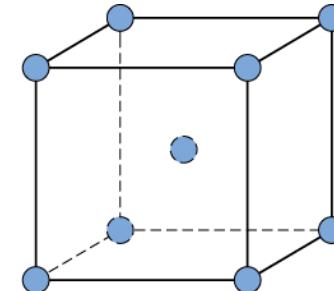
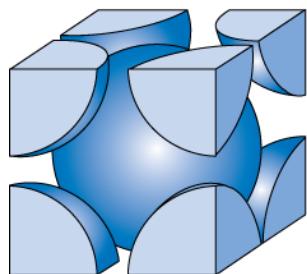
$$APF = \frac{\frac{atoms}{unit\ cell} \cdot \frac{volume}{atom}}{\frac{volume}{unit\ cell}}$$
$$APF = \frac{1 \cdot \frac{4}{3} \pi (0.5a)^3}{a^3}$$



Body-Centered Cubic Structure (BCC)

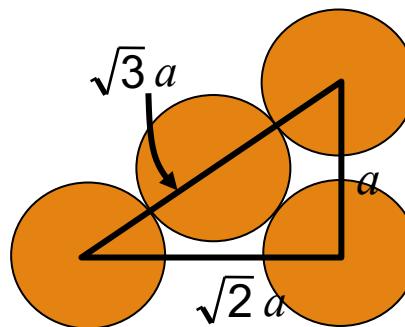
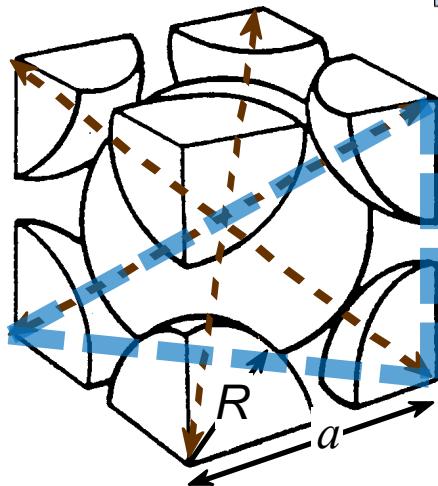


- Atoms touch each other along cube diagonals.
- ex: Cr, W, Fe (α), Tantalum, Molybdenum



• Coordination # = 8

• 2 atoms/unit cell:
1 center + 8 corners $\times 1/8$



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

$$\text{APF} = \frac{\frac{4}{3}\pi(\sqrt{3}a/4)^3}{a^3}$$

volume
atom

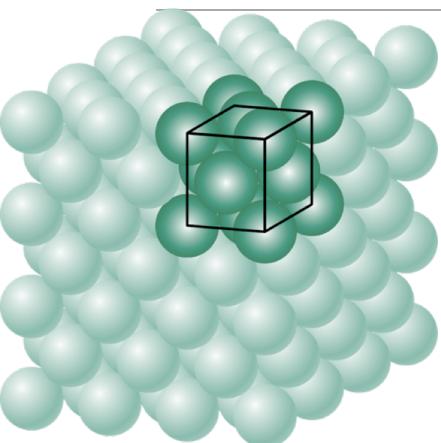
volume
unit cell

Close-packed direction

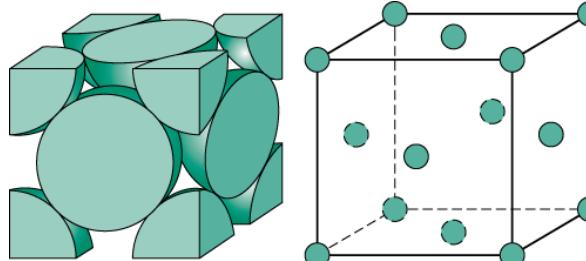
• APF for a body-centered cubic structure = 0.68



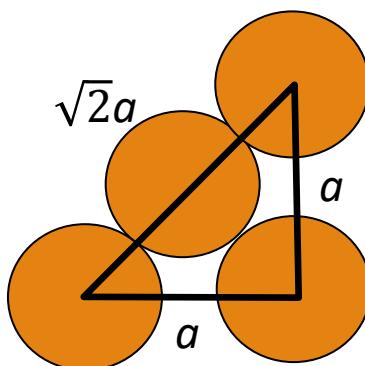
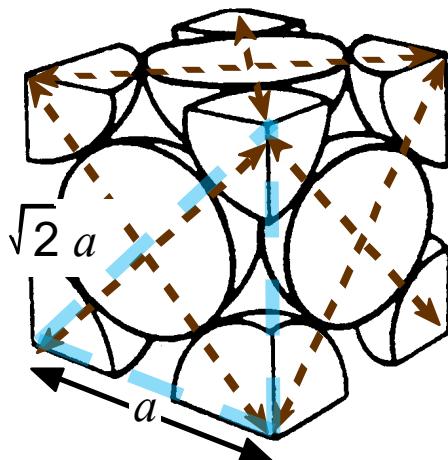
Face Centered Cubic Structure (FCC)



- 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 = $4R = \sqrt{2} a$

$$APF = \frac{\frac{atoms}{unit\ cell}}{\frac{volume}{unit\ cell}} = \frac{4 \cdot \frac{4}{3} \pi (\sqrt{2}a/4)^3}{a^3}$$

volume atom
volume unit cell

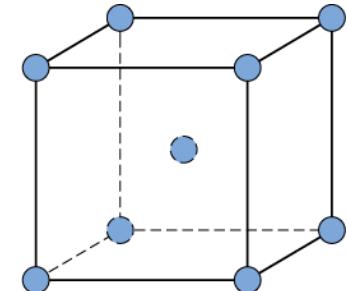
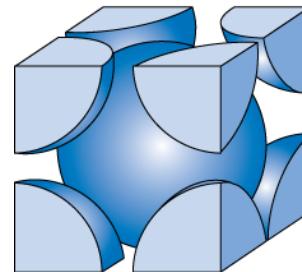
- APF for a face-centered cubic structure = 0.74



BCC, FCC 비교

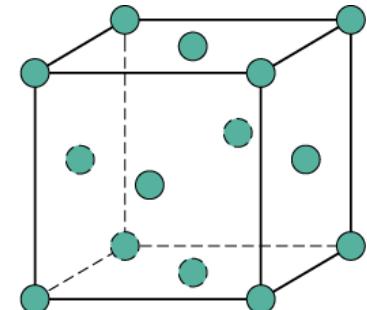
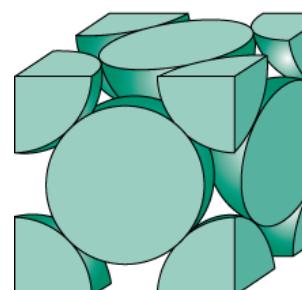
□ BCC

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



□ FCC

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



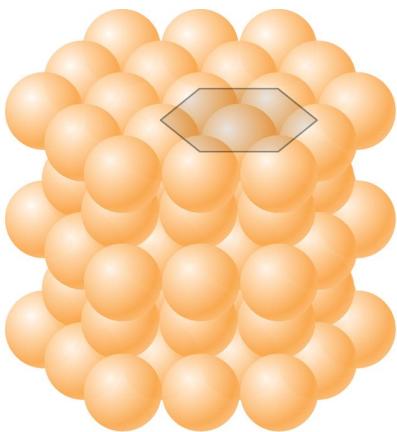
□ 대부분의 단위정의 경우 원자수 계산법

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

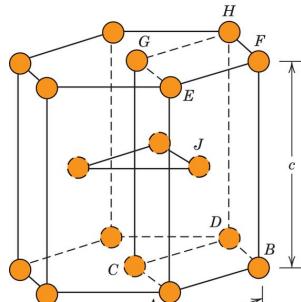
where N_i : # inside the unit cell; N_f on the faces; N_c : on the corners



Hexagonal Close-Packed Structure (HCP)



- 육각모양의 조밀 적층 (close-packed) 구조 (ABDC-EFGH를 간혹 unitcell로)
- ex: Cd, Mg, Ti, Zn



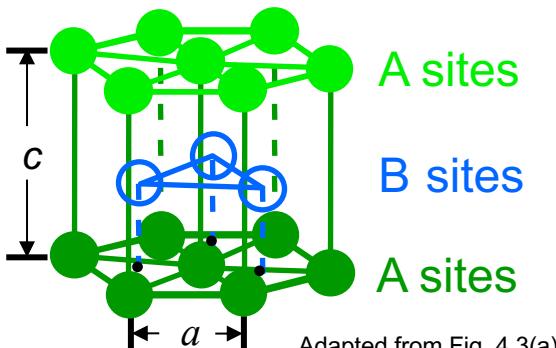
- Coordination # = 12

- 6 atoms/unit cell

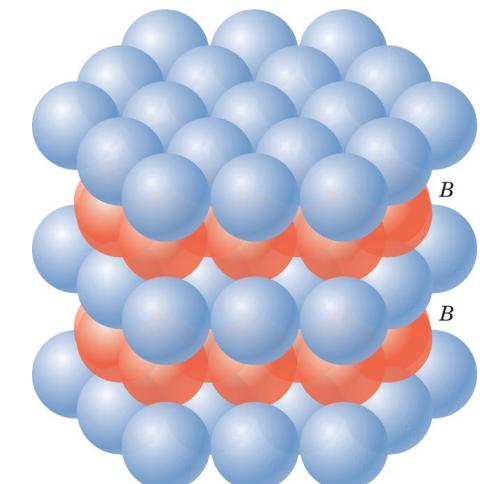
$$= 3 \times 1(\text{inside}) + 12 \times \frac{1}{6}(\text{corners}) + 2 \times \frac{1}{2}(\text{basal plane})$$

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

• 3D Projection



• 2D Projection

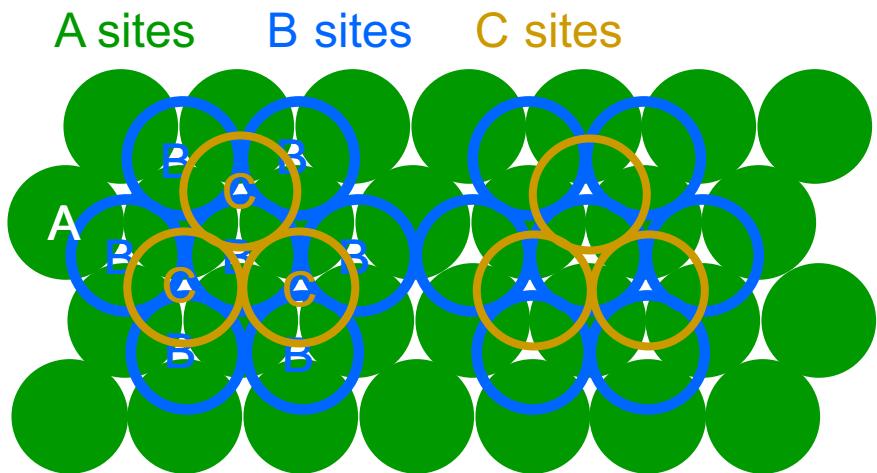


Adapted from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. I, *Structure*, p. 51. Copyright © 1964 by John Wiley & Sons, New York.



FCC Stacking Sequence (Fig 4.23a)

- ABCABC... Stacking Sequence
- 2D Projection



- FCC Unit Cell

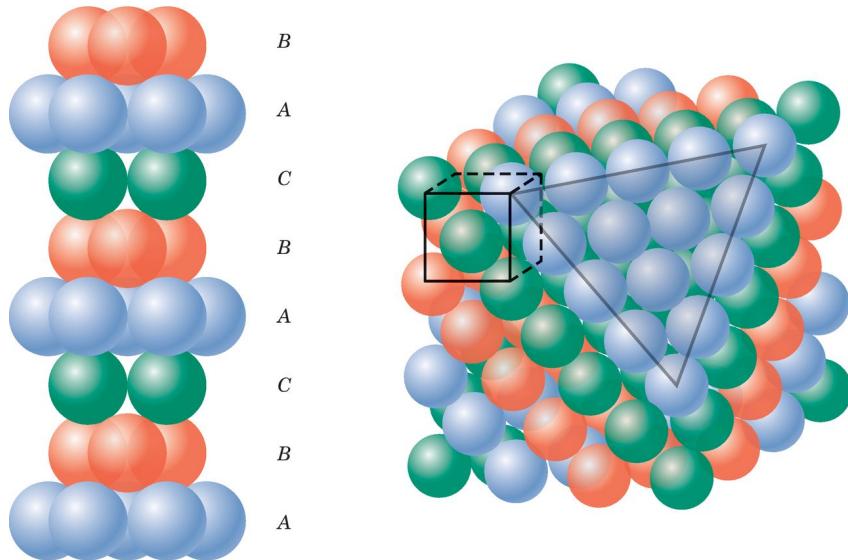
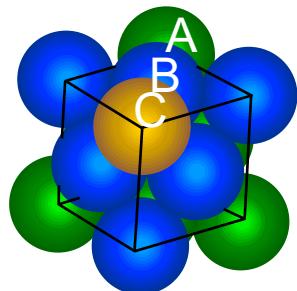


Figure (b) from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. I, *Structure*, p. 51. Copyright © 1964 by John Wiley & Sons, New York.



Theoretical Density, ρ

- Using the crystallographic structure, the density can be ‘theoretically’ calculated.

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

$$\begin{aligned} &= \frac{\text{mass per unit cell}}{\text{volume of unit cell}} \\ &= \frac{\# \text{ of Atoms per unit cell} \times \text{mass of an atom}}{\text{Vol. per unit cell}} \\ &= \frac{\# \text{ of atoms per unit cell} \times \text{mass of an atom} \times \text{Avog. \#}}{\text{Vol. per unit cell} \times \text{Avog. \#}} \end{aligned}$$

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

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)

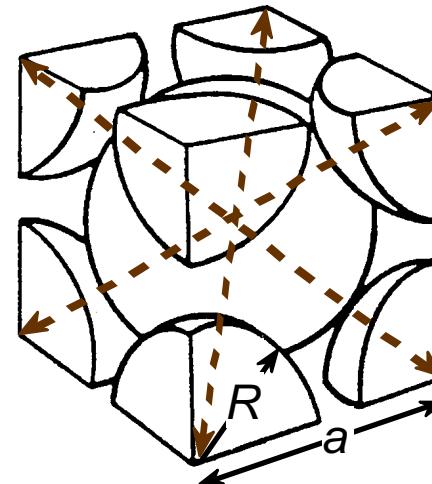
A (Atomic weight) = 52.00 g/mol

R (Atom radius) = 0.125 nm

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

Relationship between lattice parameter (a) and radius:

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



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

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

$$\rho = \frac{\frac{\text{atoms}}{\text{unit cell}} \times 2 \times 52.00}{\frac{\text{volume}}{\text{unit cell}} \times a^3 \times 6.022 \times 10^{23} \times \frac{\text{atoms}}{\text{mol}}} \times \frac{\text{g}}{\text{mol}}$$

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



Densities of Material Classes

In general

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

Why?

Metals have...

- close-packing
(metallic bonding)
- often large atomic masses

Ceramics have...

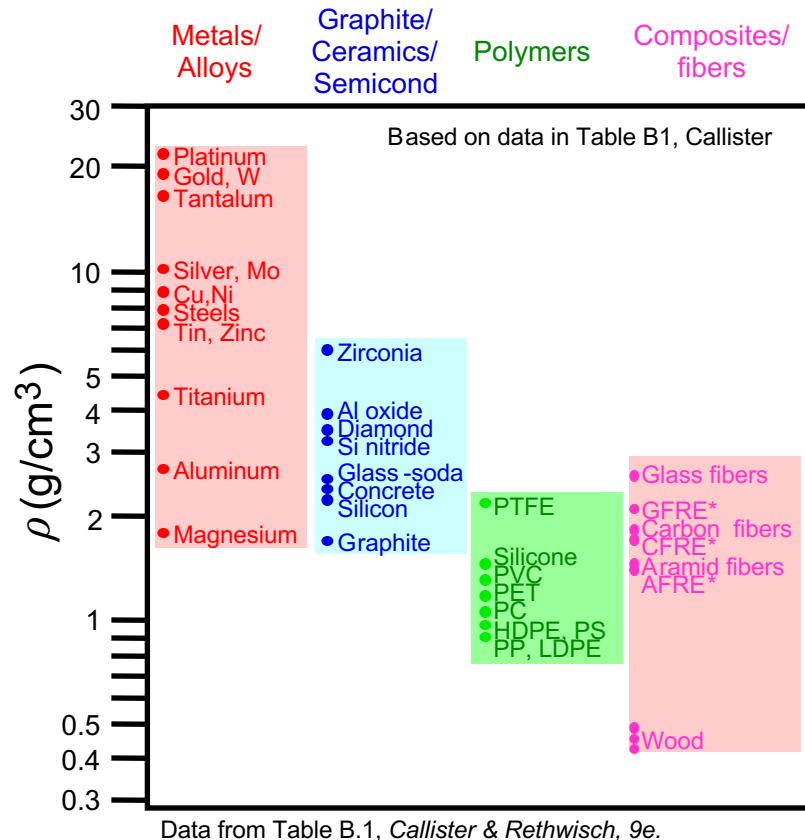
- less dense packing
- often lighter elements

Polymers have...

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

Composites have...

- intermediate values



Polymorphism

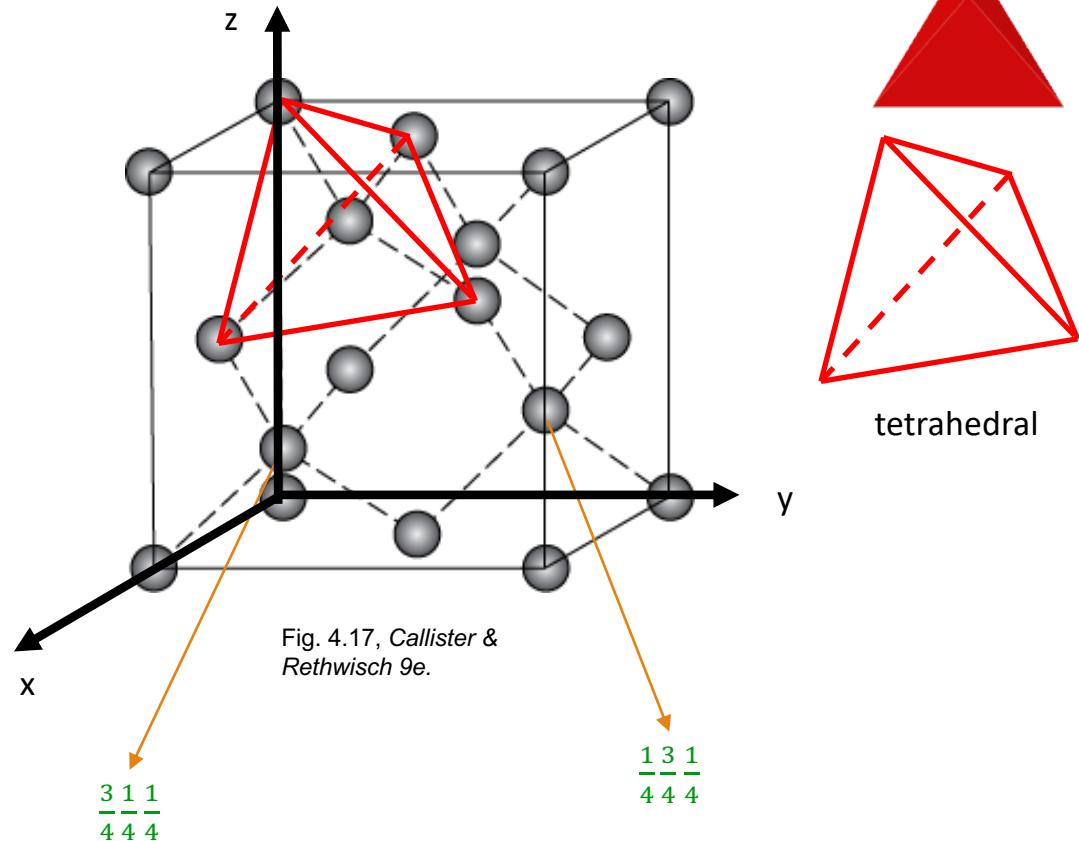
- 한 금속 원소가 하나 이상의 결정 구조를 가질 수 있을 때.
- 같은 금속 원소지만 다른 결정 구조를 가질 수 있는 현상을 “동질이상” (polymorphism)이라 한다.
- 단일 고체에서 이러한 현상을 동소체 (allotropy)라 함.
- 결정 구조의 압력, 온도 의존성.
- 탄소/다이아 몬드
- 철 – BCC (대부분의 철, 강) or FCC (대부분의 스테인레스 강) or even HCP
- Ti- alpha/beta



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.



Polymorphic Forms of Carbon

Graphite

- layered structure – parallel hexagonal arrays of carbon atoms

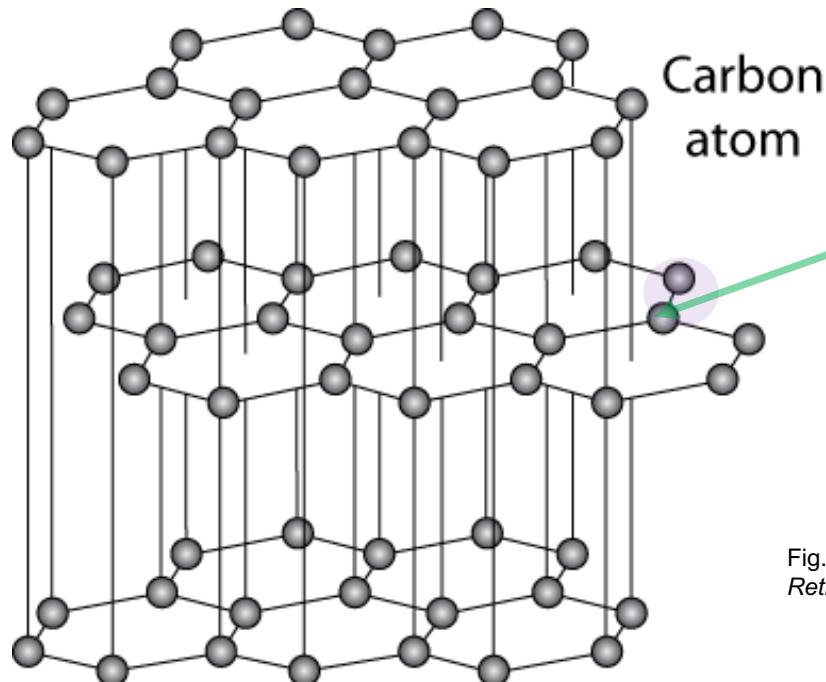
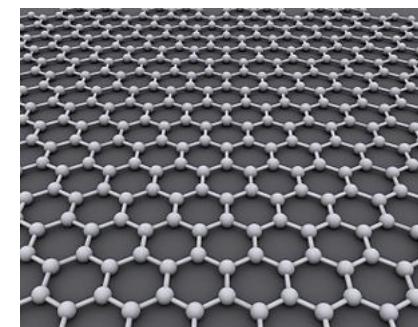


Fig. 4.18, Callister & Rethwisch 9e.

sp^2 hybrid orbital
(공유 결합)

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

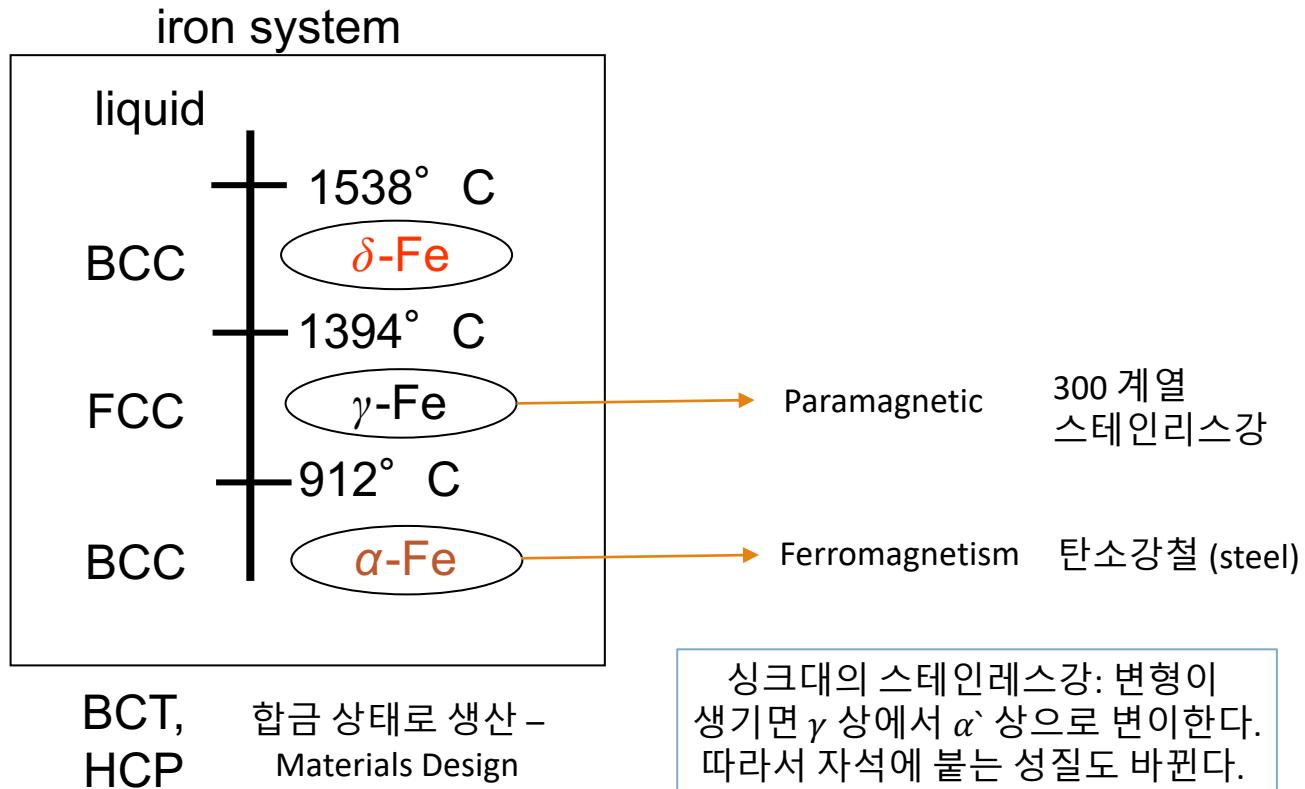


- weak van der Waal's forces between layers
- planes slide easily over one another -- good (solid) lubricant



Polymorphism of iron

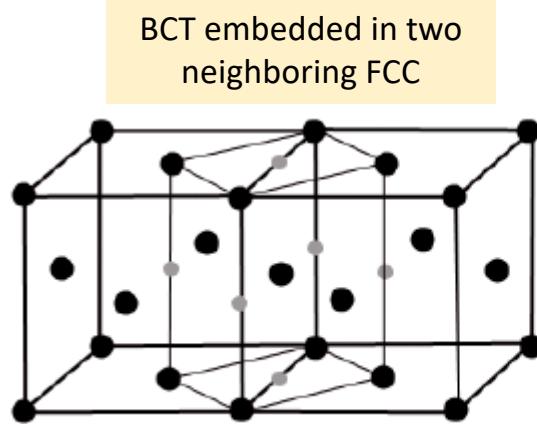
Two or more distinct crystal structures for the same material (allotropy/polymorphism)



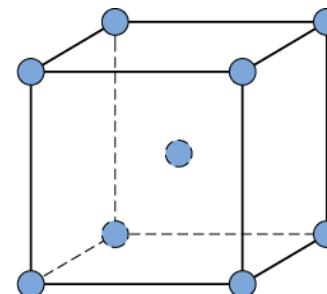
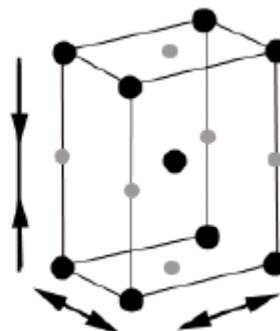
Polymorphism of iron: phase transformation

$\gamma\text{-Fe}$  $\alpha\text{-Fe}$
FCC BCC

온도에 따라 에너지적으로 안정된
결정구조가 달라진다.



Distorting BCT in a certain way can result in BCC



고체 상태의 FCC와 BCT의 유사성

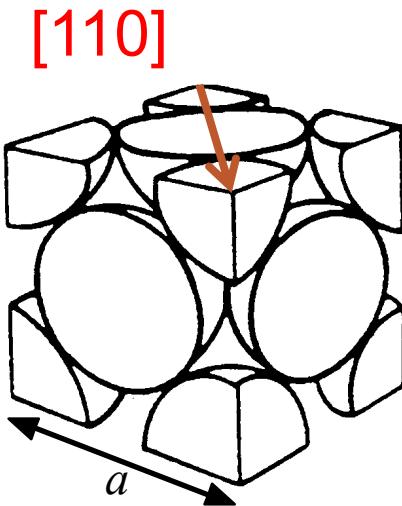


Linear Density

□ Linear Density of Atoms \equiv LD =

Number of atoms

Unit length of direction vector



ex: linear density of Al in [110] direction
 $a = 0.405 \text{ nm}$

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



Planar Density of (100) Iron

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

At $T < 912^{\circ}\text{C}$, iron (Fe) has the BCC structure.

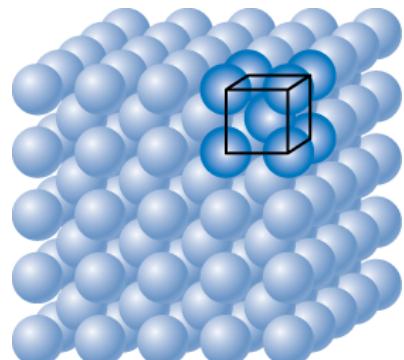
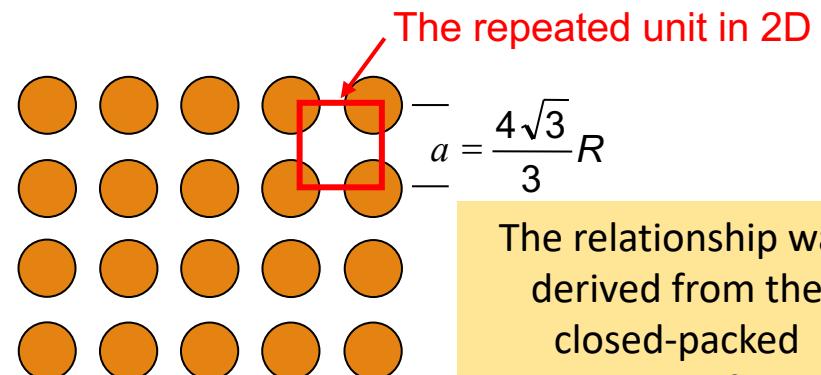


Fig. 4.2(c), Callister & Rethwisch 9e [from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. I, *Structure*, p. 51. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.]

(100)



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

Radius of iron $R = 0.1241 \text{ nm}$

of Atoms having their centers lying on the plane

Repeated unit in 2D

Planar Density

$$\frac{1}{a^2}$$

$$\left(\frac{4\sqrt{3}}{3}R\right)^2$$

atoms
 nm^2

$1.2 \times 10^{19} \frac{\text{atoms}}{\text{m}^2}$

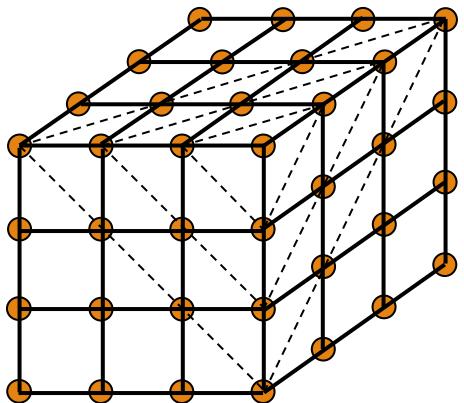
Area of atoms within the repeated unit

Repeated unit in 2D



Planar Density of (111) Iron

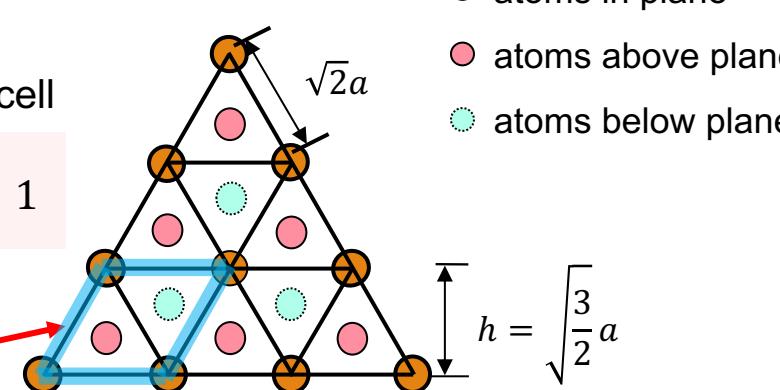
What is PD of (111)?



1 atom in plane / unit surface cell

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

The repeated unit



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

$$\text{Planar Density} = \frac{1}{\frac{16\sqrt{3}}{3} R^2} = 7.0 \frac{\text{atoms}}{\text{nm}^2} = 0.70 \times 10^{19} \frac{\text{atoms}}{\text{m}^2}$$



Crystals as Building Blocks

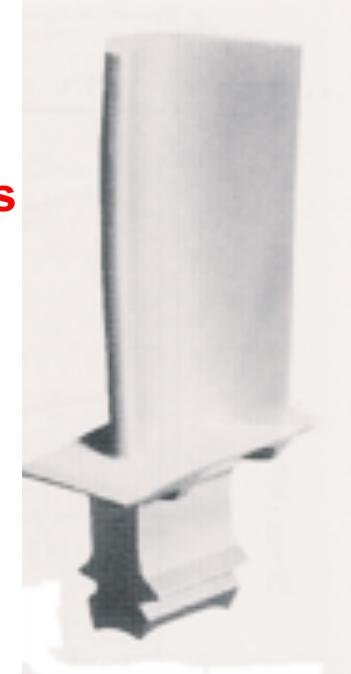
- Some engineering applications require single crystals:

-- **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.

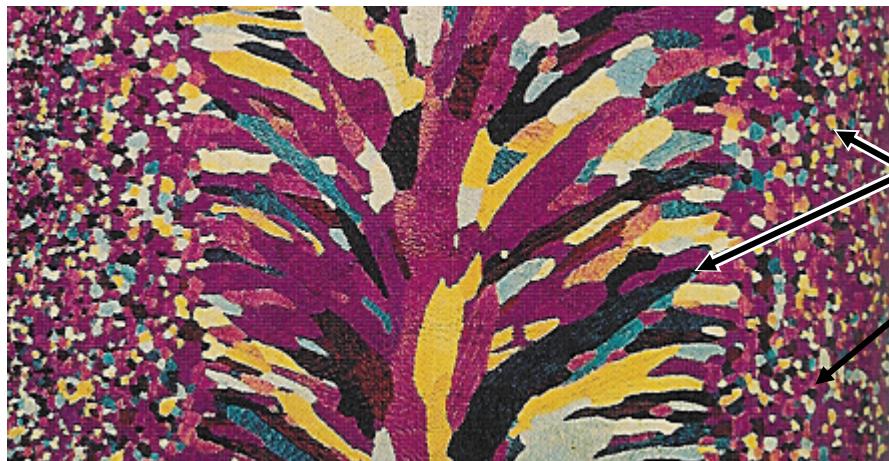


(Courtesy P.M. Anderson)



Polycrystals

- Most engineering materials are **polycrystals**.



1 mm

Isotropic

Anisotropic
(morphological texture)

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

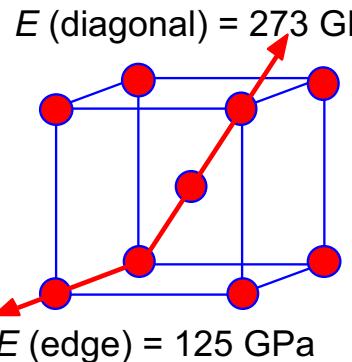
- Nb-Hf-W plate with an electron beam weld.
- Each "grain" is a single crystal.
- If grains are **randomly oriented** and **equi-axed**, overall component properties are **NOT** directional.



Single vs Polycrystals

• Single Crystals

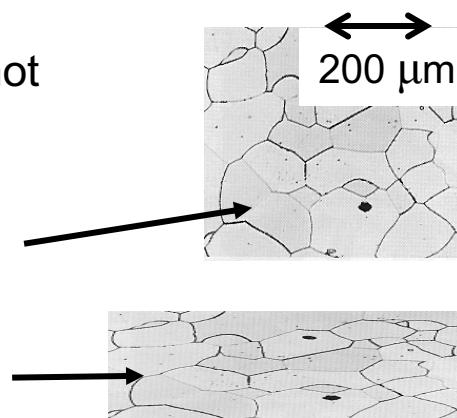
- Properties vary with direction: **anisotropic**.
- Example: the modulus of elasticity (E) in BCC iron:



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**.
($E_{\text{poly iron}} = 210 \text{ GPa}$)
- 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).]

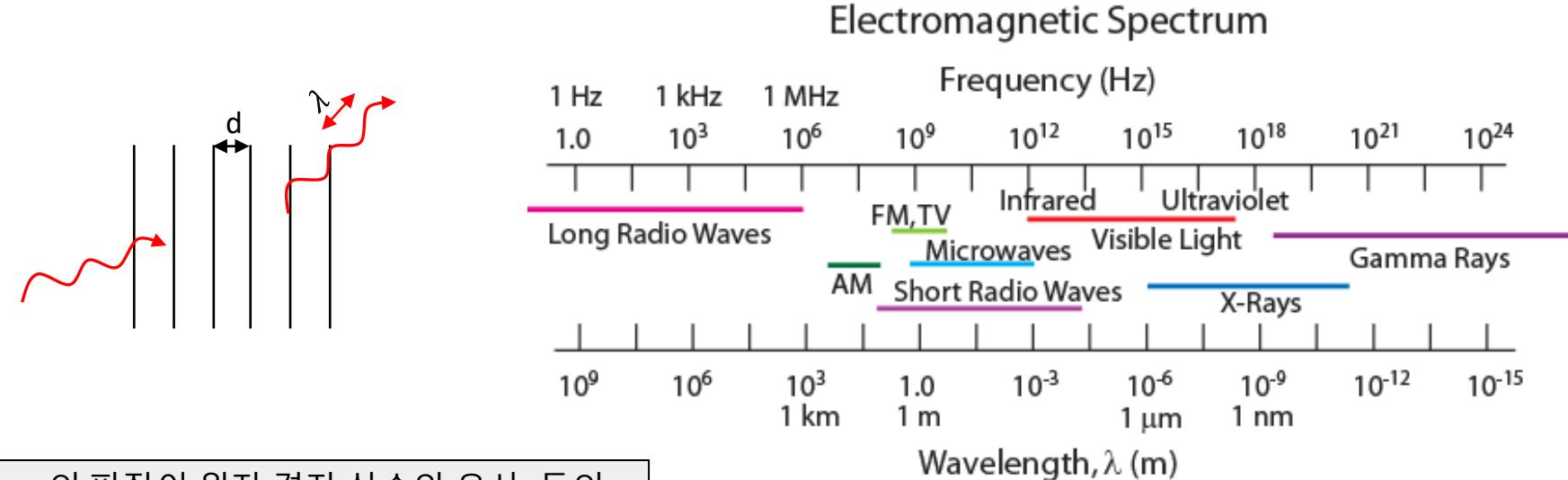
Texture:

- 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 판일 파장(진동수-1)으로
이루어진 electromagnetic wave

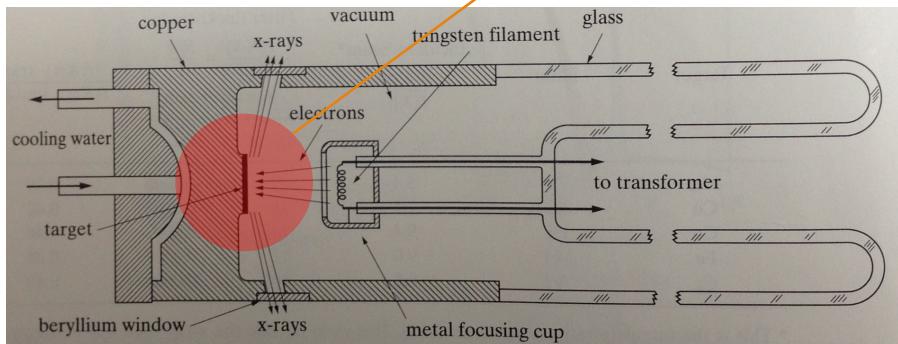
(Low-power) 단색 X-ray는 원자의 전자 구조를 사용해서 만들어 낸다.
(혹은) Synchrotron 시설에서도 만들 수 있다.



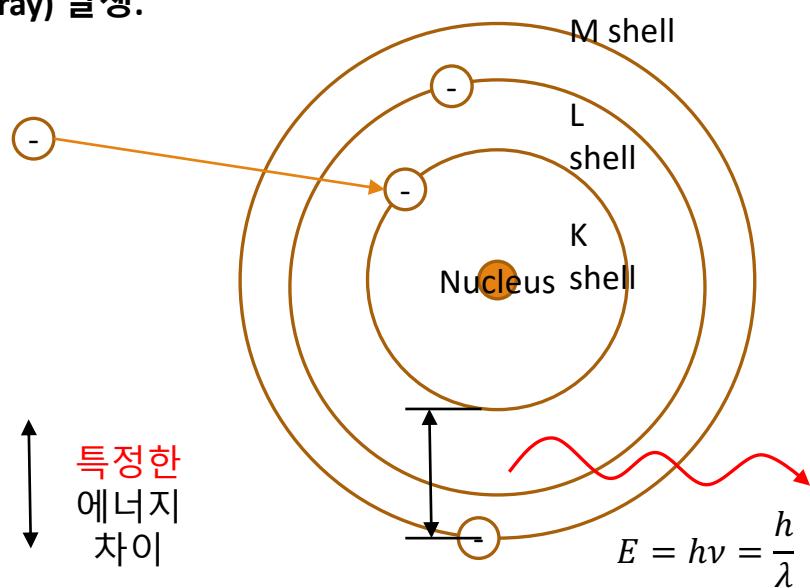
Monochromatic X-ray



X-ray tube



Target으로 쓰이는 재료마다 특성 X-ray
(characteristic X-ray) 발생.



외부의 전자가 각 주
에너지각에
존재하는 전자들을
knock-off

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

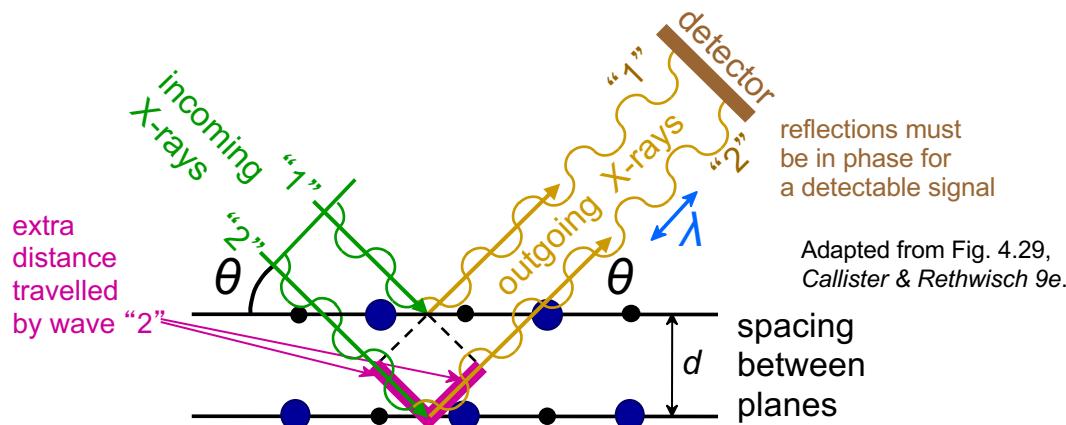
그러한 전자가 한
shell에서 다른 shell로
이동하며 EM으로
방출 (X-ray)

원자의 전자 구조는
'고유한' 성질을
가지므로 단색의 x-
ray 발생



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

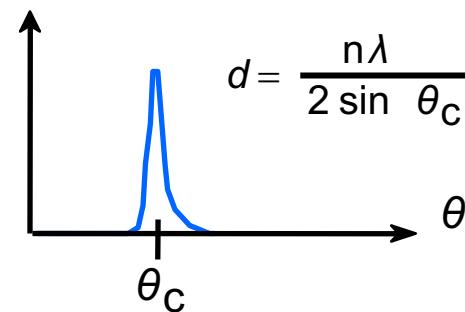
- Incoming X-rays **diffract** from crystal planes.



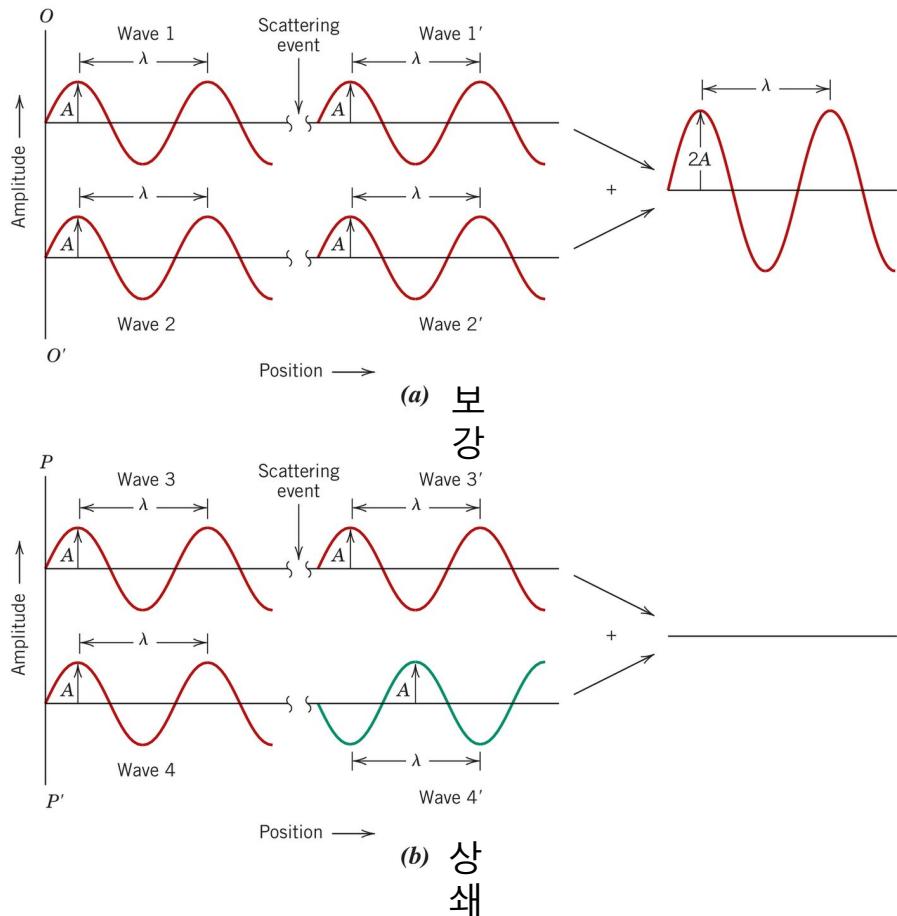
Adapted from Fig. 4.29,
Callister & Rethwisch 9e.

Measurement of critical angle, θ_c , allows computation of planar spacing, d through the use of Bragg's law

X-ray intensity
(from detector)



X-Ray Diffraction rule



결정구조에 면에 따라 보강이나 상쇄가 일어날 수 있다. 예를 들면, BCC의 (100) 면은 회절이 안되나 (200) 면은 된다.

(100)면과 (200) 면이 다른면인가?

X-ray crystallography community에서는 (100)면과 (200) 면을 결정면간 거리가 다른 것을 바탕으로 구분한다.

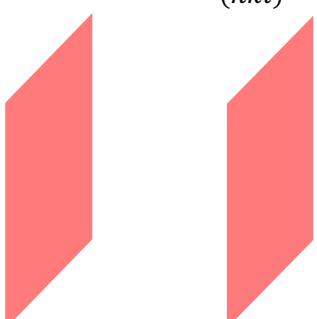
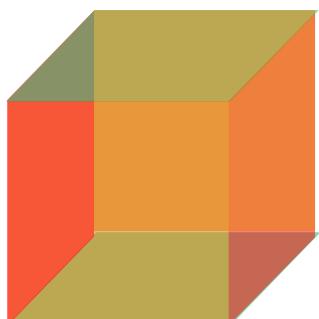


X-Ray Diffraction rule

(100)면과 (200) 면이 다른면인가?

X-ray community 에서는 (100)면과 (200)
면을 결정면간 거리가 다른 것을
바탕으로 구분한다.

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



$d_{(hkl)}$



In cubic crystal structure, $d_{(hkl)} = \frac{a}{\sqrt{h^2+k^2+l^2}}$ $d_{(100)} = 2 d_{(200)}$



X-Ray Diffraction rule

모든 crystallographic plane에서 회절 현상이 일어나는 것은 아니다.

Bragg's law는 필요조건

또 다른 조건들이 있다.

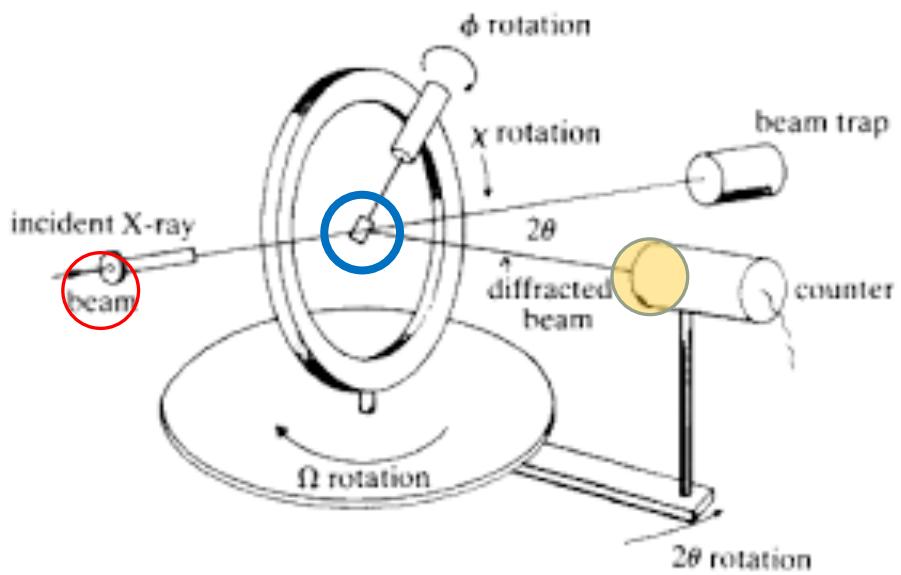
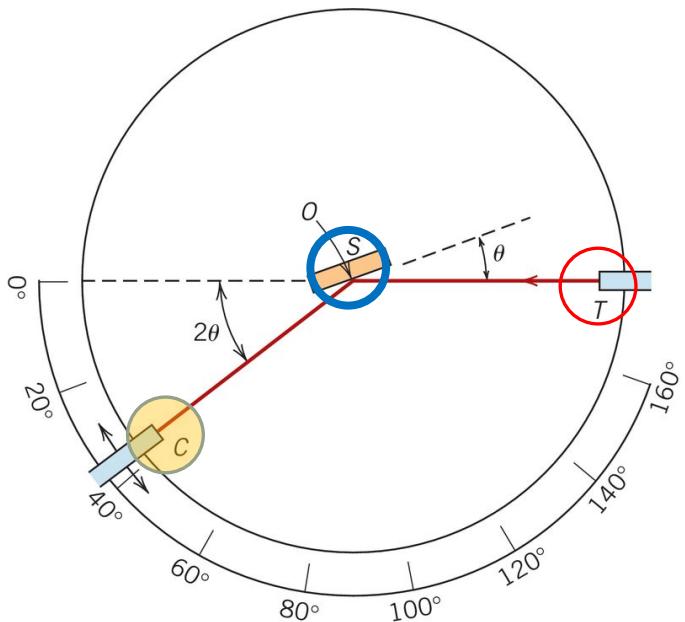
Table 4.6

X-Ray Diffraction
Reflection Rules and
Reflection Indices
for Body-Centered
Cubic, Face-Centered
Cubic, and Simple
Cubic Crystal
Structures

<i>Crystal Structure</i>	<i>Reflections Present</i>	<i>Reflection Indices for First Six Planes</i>
BCC	$(h + k + l)$ even	110, 200, 211, 220, 310, 222
FCC	h, k , and l either all odd or all even	111, 200, 220, 311, 222, 400
Simple cubic	All	100, 110, 111, 200, 210, 211



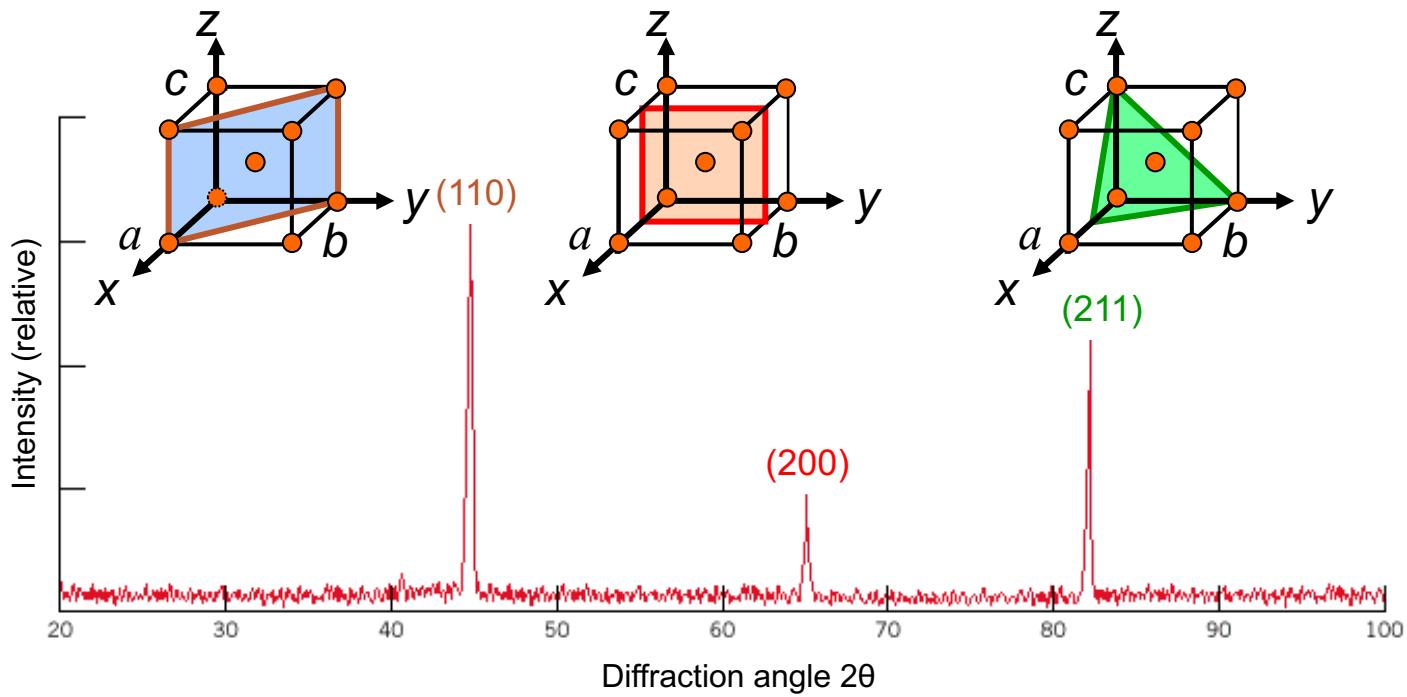
X-Ray Diffractometer



Goniometer: 한 공간에서 여러 방위로
시편을 놓기 위한 장치



X-Ray Diffraction Pattern



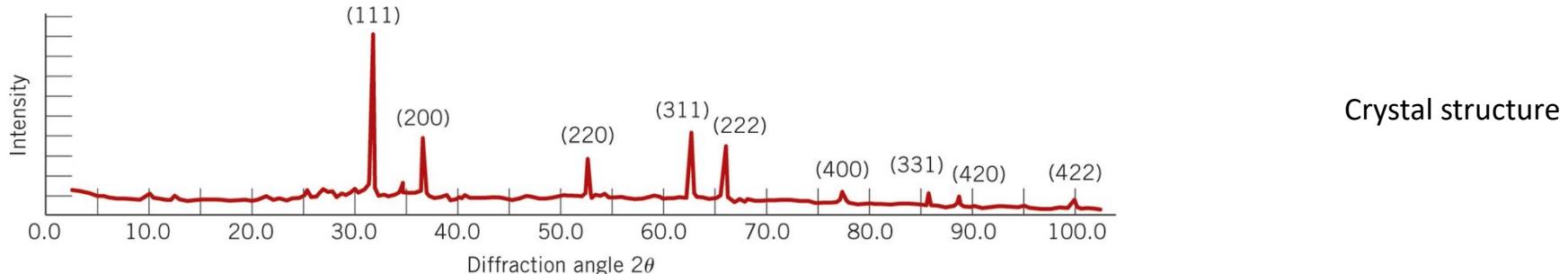
Diffraction pattern for polycrystalline α -iron (BCC)

Adapted from Fig. 3.22, Callister 8e.

Increase in interplanar
displacing leads to
increase in diffraction
angle.

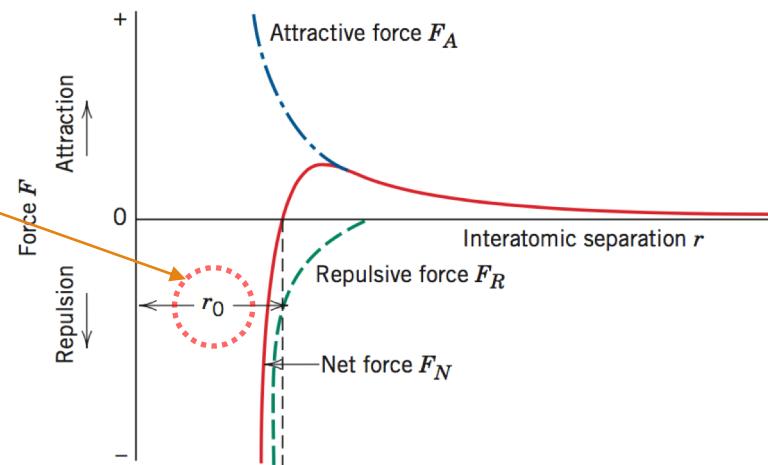
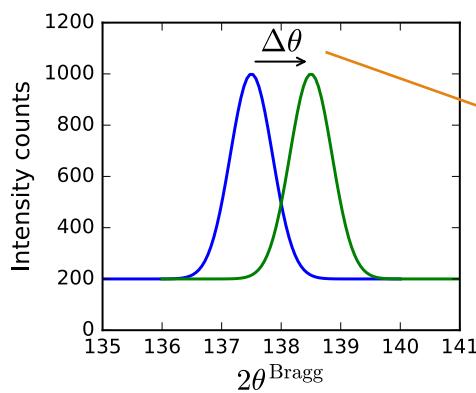


X-Ray diffraction and its applications in Materials Science



Courtesy of Wesley L. Holman.

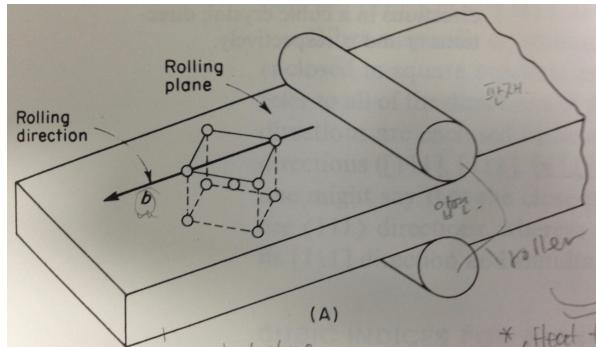
Crystal structure



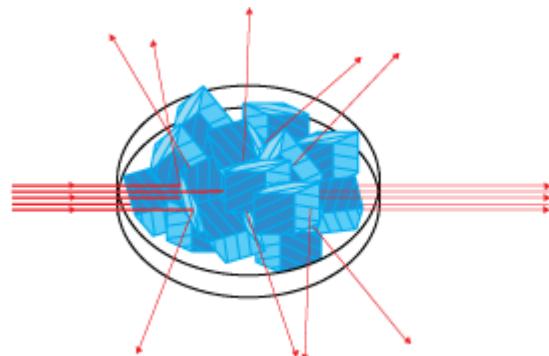
Residual stress measurement



X-Ray diffraction and its applications in Materials Science

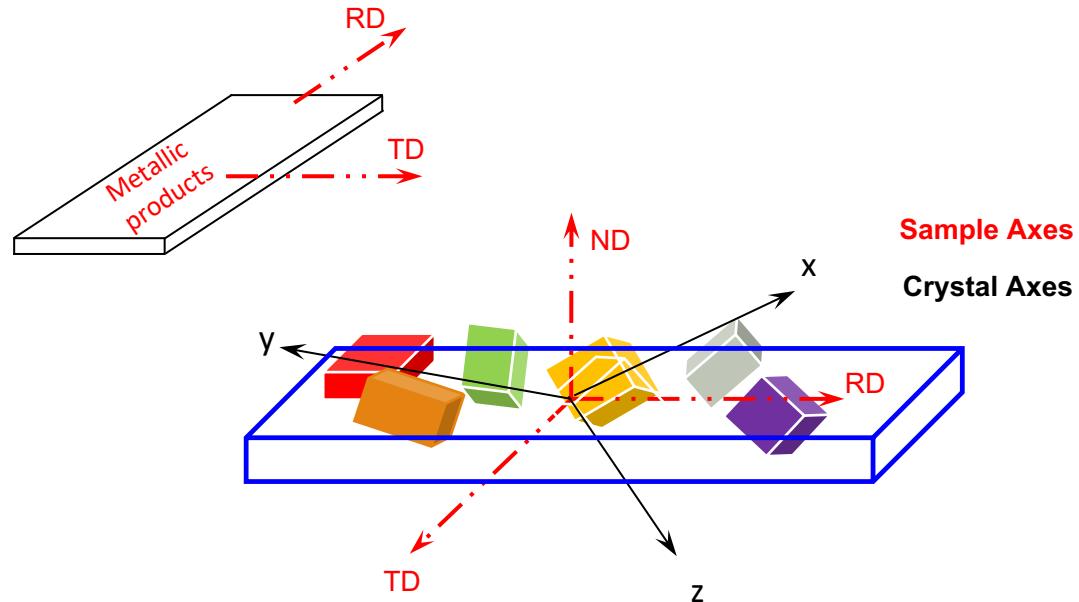


집합 조직의 측정



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

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



역으로, 특정방향으로 diffraction이 강하게 발생한다면 polycrystal의 방위가 특정방향으로 많이 놓여져있다 (texture가 존재)

