2020 Fall

Introduction to Materials Science and Engineering

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Contents for previous class

Chapter 4: Imperfections in Solids

I. Point defects

- Point defects in metals/ceramics/polymers, impurities in solids

- Equilibrium concentration varies with temperature!

$$\frac{N_v}{N} = \exp\left(\frac{-Q_v}{kT}\right)$$

- Two outcomes if impurity (B) added to host (A):
  - Solid solution of B in A (i.e., random dist.) _ **Hume-Rothery Rules**
  - Solid solution of B in A plus particles of a new phase (usually for a larger amount of B) _ **Precipitation!**

➢ Weight % $C_B = \frac{\text{mass of B}}{\text{total mass}} \times 100$ ➢ Atom % $C'_B = \frac{\text{\# atoms of B}}{\text{total \# atoms}} \times 100$

- Imperfection in Ceramics: Electroneutrality (charge balance) must be maintained when impurities are present.

- Point defects in polymer: defects due in part to chain packing errors and impurities such as chain ends and side chains

Contents for today's class

Chapter 4: Imperfections in Solids

I. Point defects

- Point defects in metals/ceramics/polymers, impurities in solids

II. Dislocations-Linear defects

- Edge/ Screw/ Mix dislocation

III. Interfacial defects

- External surfaces/ Grain boundaries/ Phase boundaries (stacking fault)/ Twin boundaries/ domain boundaries

IV. Bulk or Volume defects

- pores/ cracks/ foreign inclusions, and other phases

V. Microscopic Examination

- Basic concepts of microscopy
- Microscopic techniques : Optical microscopy (Grain-size determination) / Electron microscopy/ Scanning probe microscopy

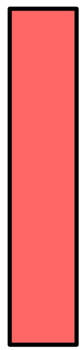
II. Line Defects

Dislocations:

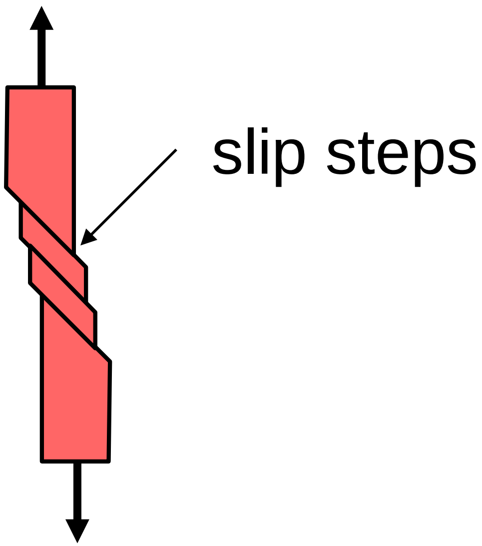
- are line defects,
- slip between crystal planes result when dislocations move,
- produce permanent (plastic) deformation.

Schematic of Zinc (HCP):

- before deformation



- after tensile elongation



Imperfections in Solids

Linear Defects (Dislocations)

- Are one-dimensional defects around which atoms are misaligned

- Edge dislocation:
  - extra half-plane of atoms inserted in a crystal structure
  - **b** perpendicular ($\perp$) to dislocation line

- Screw dislocation:

Burger's vector, **b**: measure of lattice distortion

- spiral planar ramp resulting from shear deformation
- **b** parallel ($\|$) to dislocation line

Imperfections in Solids

Edge Dislocation

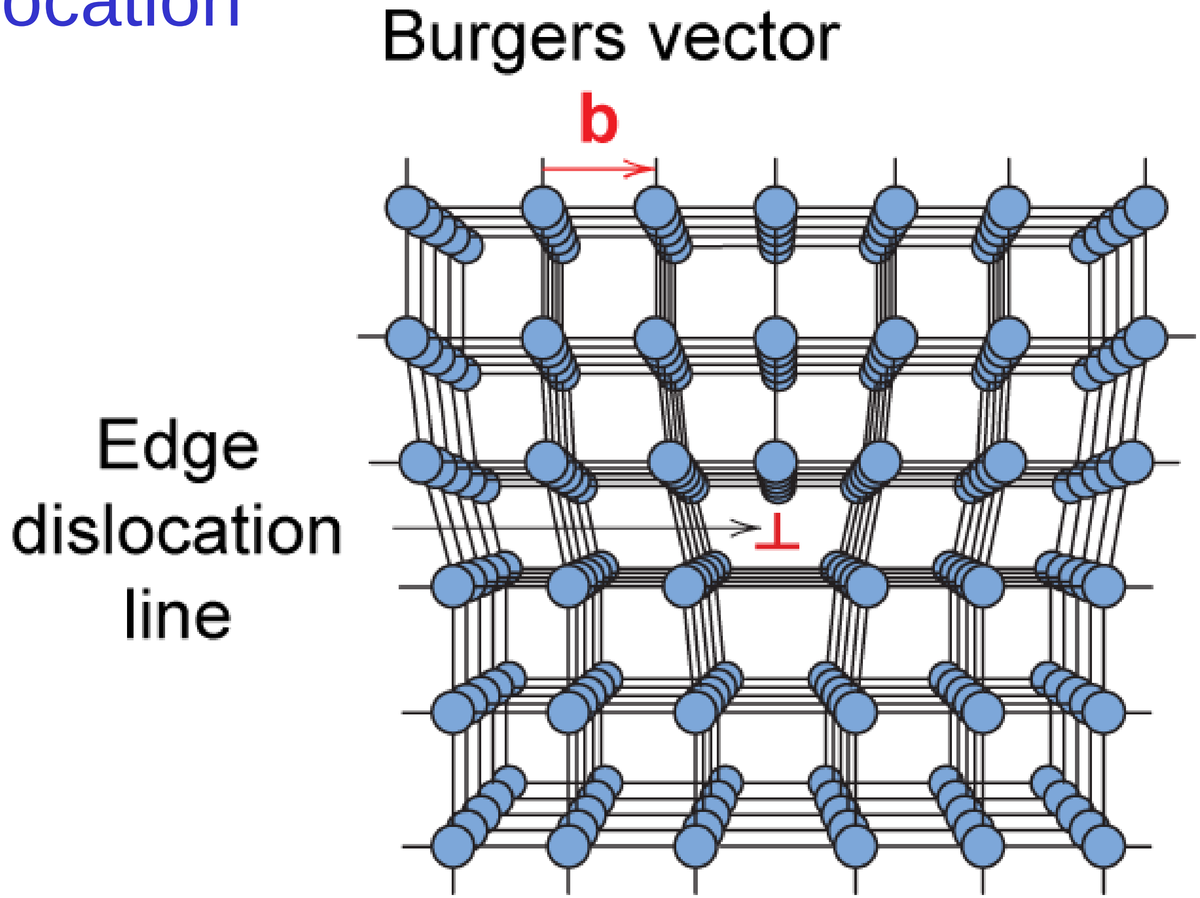
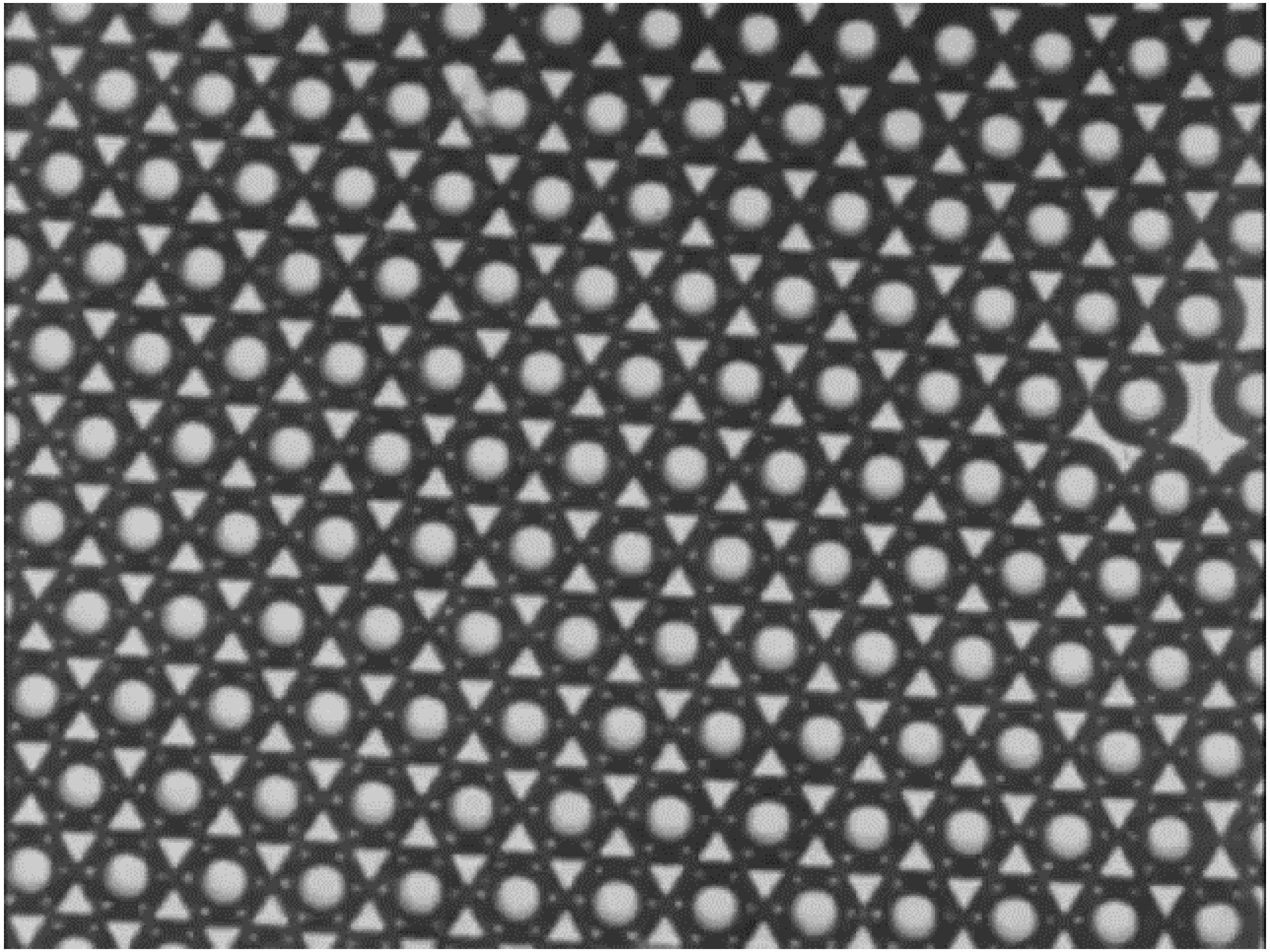
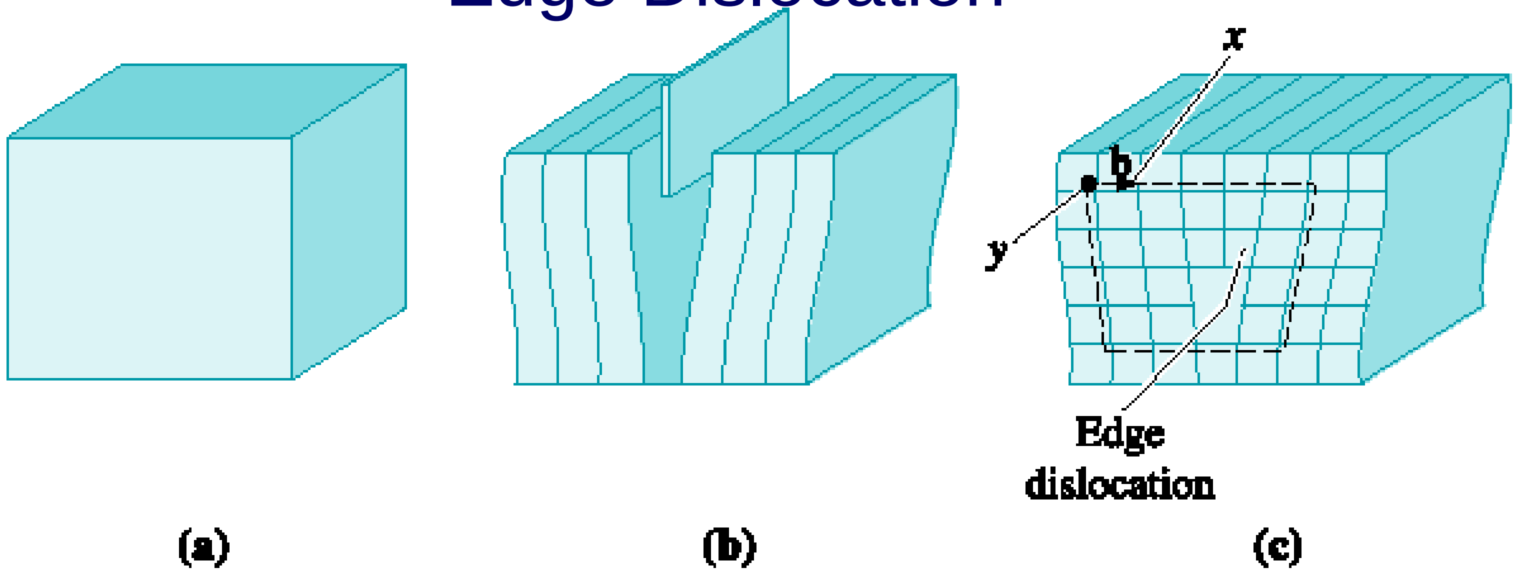


Fig. 6.9, *Callister & Rethwisch 9e.* (Adapted from A. G. Guy, Essentials of Materials Science, McGraw-Hill Book Company, New York, NY, 1976, p. 153.)

Burgers vector determination



Edge Dislocation



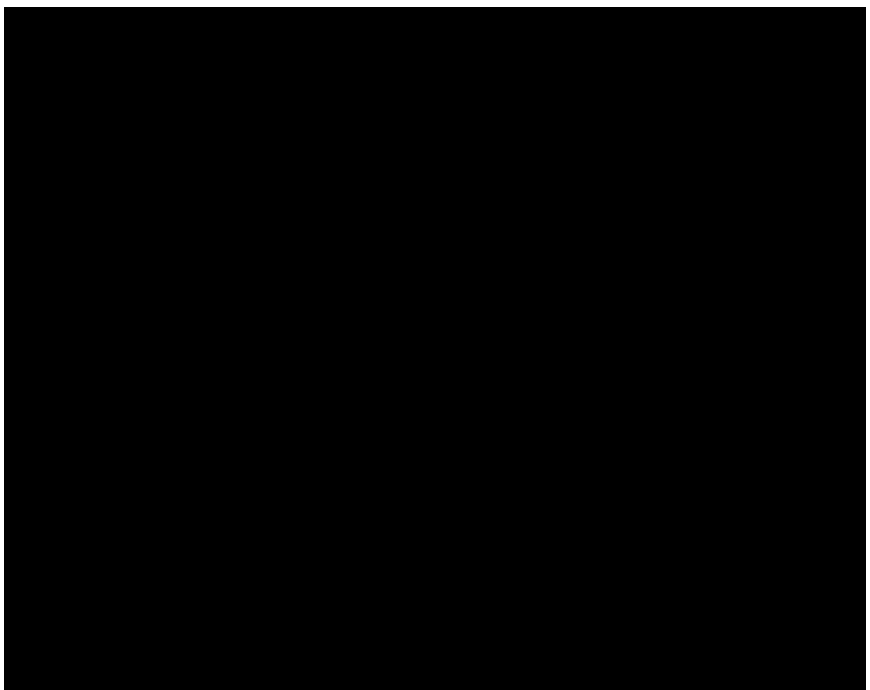
- The perfect crystal in (a) is cut and an extra plane of atoms is inserted (b). The bottom edge of the extra plane is an edge dislocation (c).

- A Burgers vector b is required to close a loop of equal atom spacings around the edge dislocation → magnitude & direction of the lattice distortion

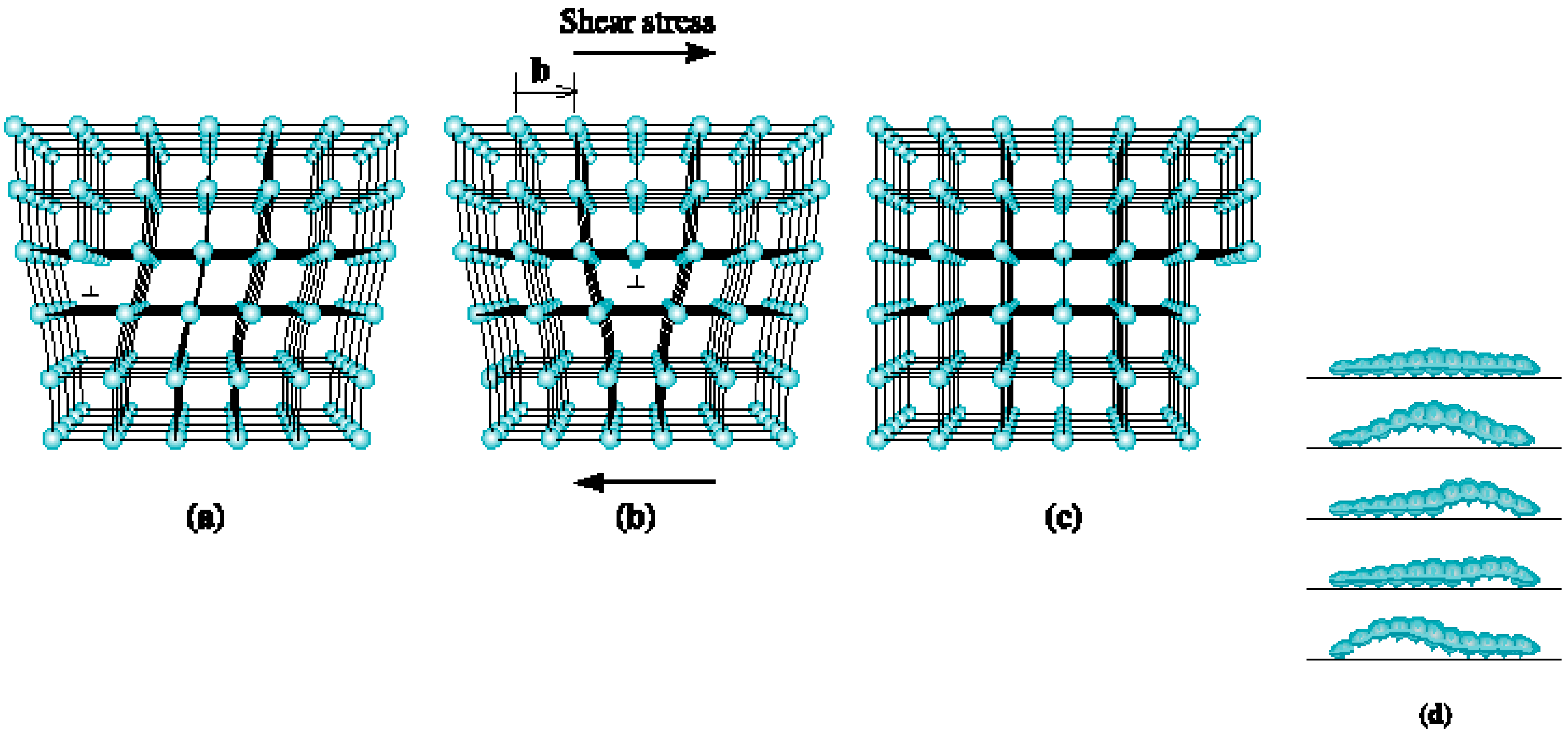
- Burgers vector $b \perp$ dislocation line

Bond Breaking and Remaking

- Dislocation motion requires the successive bumping of a half plane of atoms (from left to right here)
- Bonds across the slipping planes are broken and remade in succession

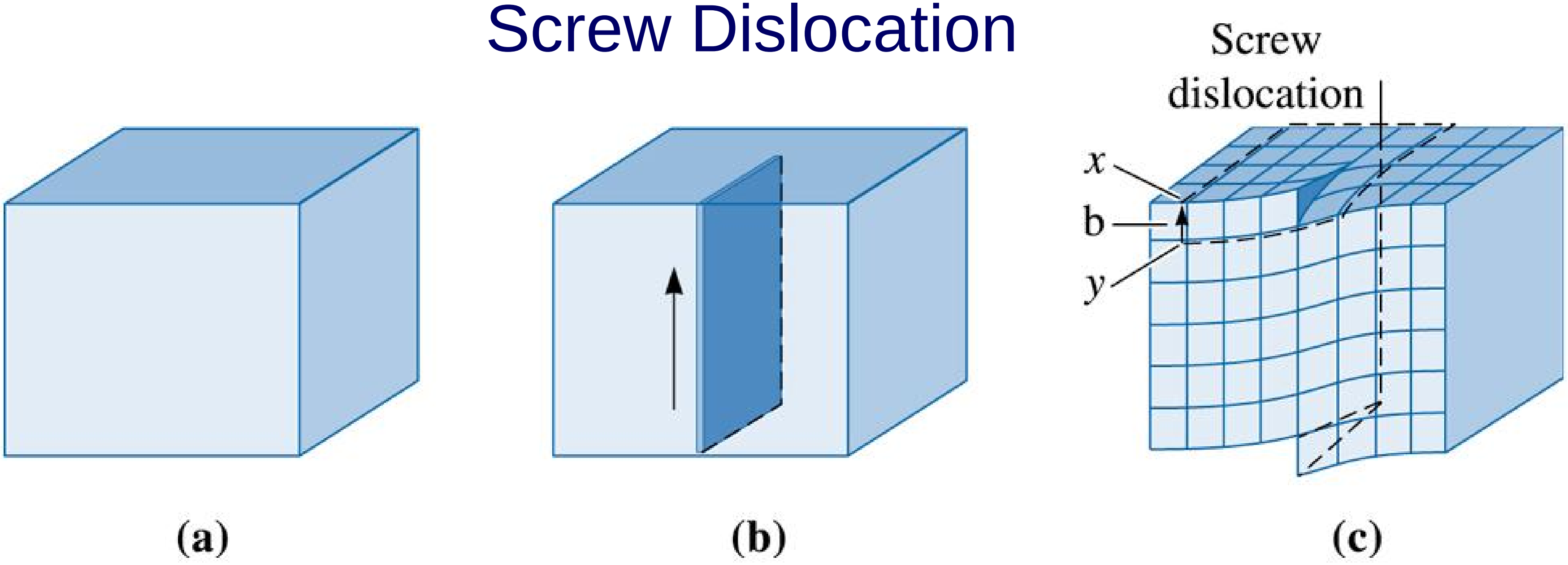


Atomic view of edge dislocation motion from left to right as a crystal is sheared.



(a) When a shear stress is applied to the dislocation in (a), the atoms are displaced, causing the dislocation to move one Burgers vector in the slip direction (b). Continued movement of the dislocation eventually creates a step (c), and the crystal is deformed. (d) Motion of caterpillar is analogous to the motion of a dislocation.

Screw Dislocation



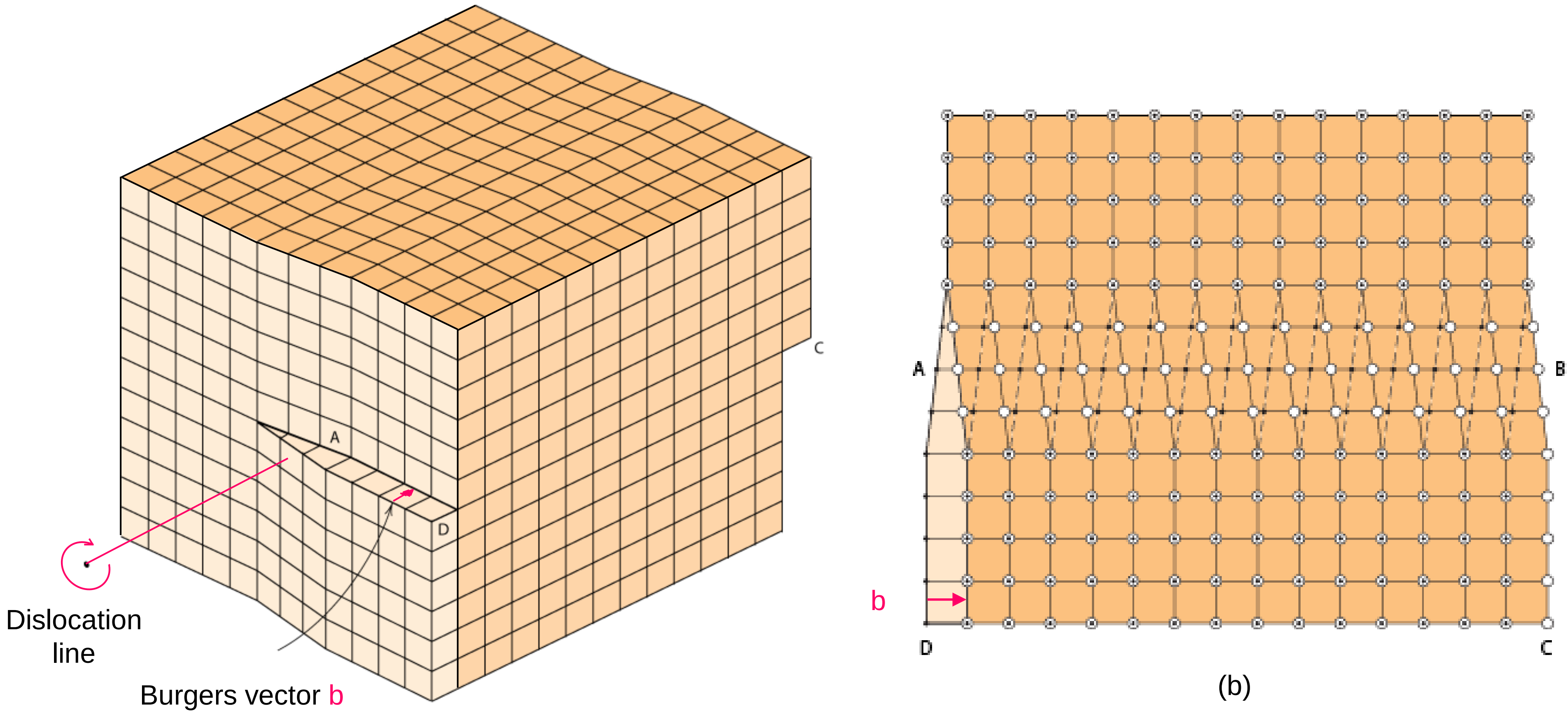
➢ The perfect crystal (a) is cut and sheared one atom spacing, (b) and (c). The line along which shearing occurs is a screw dislocation.

➢ A Burgers vector *b* is required to close a loop of equal atom spacings around the screw dislocation → magnitude & direction of the lattice distortion

➢ Burgers vector *b* // dislocation line

Imperfections in Solids

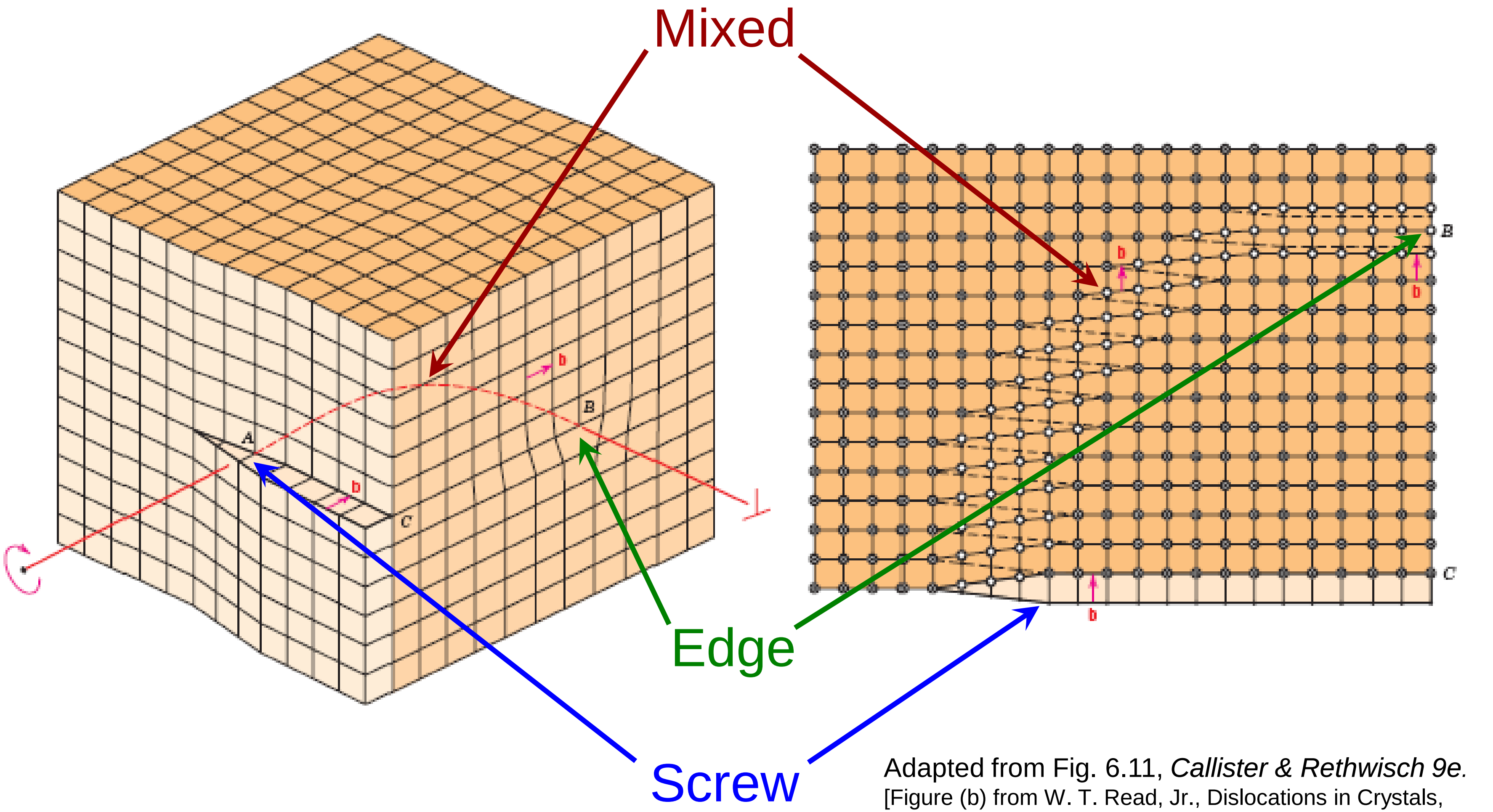
Screw Dislocation



(a) (b)

Adapted from Fig. 6.10, *Callister & Rethwisch 9e.*
[Figure (b) from W. T. Read, Jr.,Dislocations in Crystals, McGraw-Hill Book Company, New York, NY, 1953.]

Edge, Screw, and Mixed Dislocations



Adapted from Fig. 6.11, *Callister & Rethwisch 9e.*
[Figure (b) from W. T. Read, Jr., Dislocations in Crystals, McGraw-Hill Book Company, New York, NY, 1953.]

Imperfections in Solids

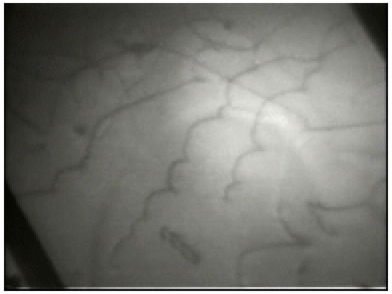
Dislocations are visible in electron micrographs

Fig. 6.12, *Callister & Rethwisch 9e.*
(Courtesy of M. R. Plichta, Michigan Technological University.)

Dislocation density

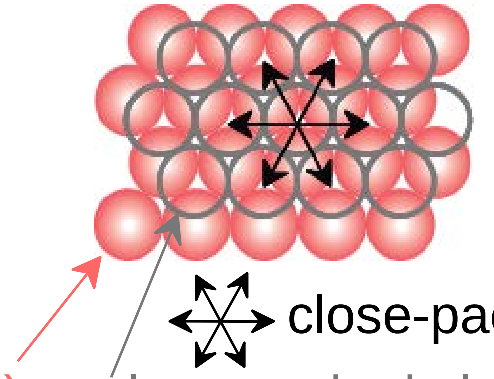
- Carefully solidified metal 10^3 mm^{-2}
- Heavily deformed metals $10^9 \sim 10^{10}$ mm^{-2}
- Heavily deformed metals after heat treatment

  $10^5 \sim 10^6$ mm^{-2}
- ceramics $10^2 \sim 10^4$ mm^{-2}
- Si wafer $0.1 \sim 1$ mm^{-2}



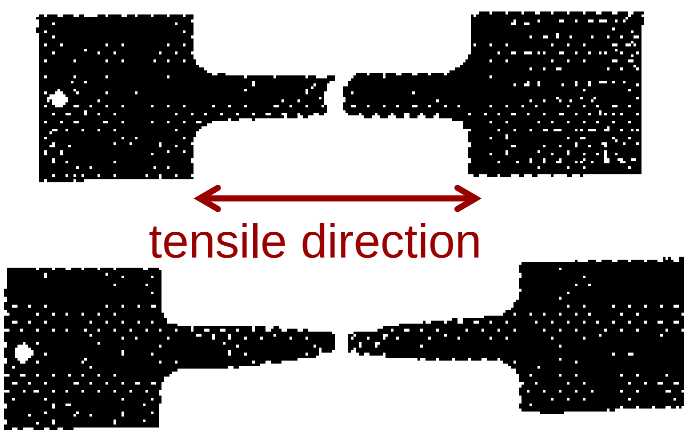
Dislocations & Crystal Structures

- Structure: close-packed planes & directions are preferred.



- Comparison among crystal structures:
  FCC: many close-packed planes/directions;
  HCP: only one plane, 3 directions;
  BCC: none

- Specimens that were tensile tested.



III. Planar Defects

(1) External surface

(2) grain boundary

(3) phase boundary (stacking fault)

(4) twin boundary

(5) domain boundary

(1) Surface Defects → Catalysts

- A catalyst increases the rate of a chemical reaction without being consumed
- Active sites on catalysts are normally surface defects

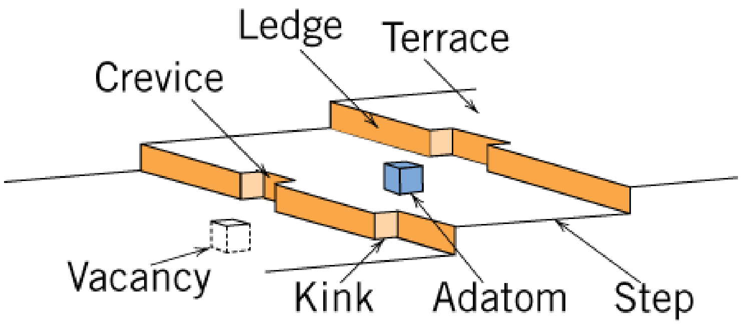
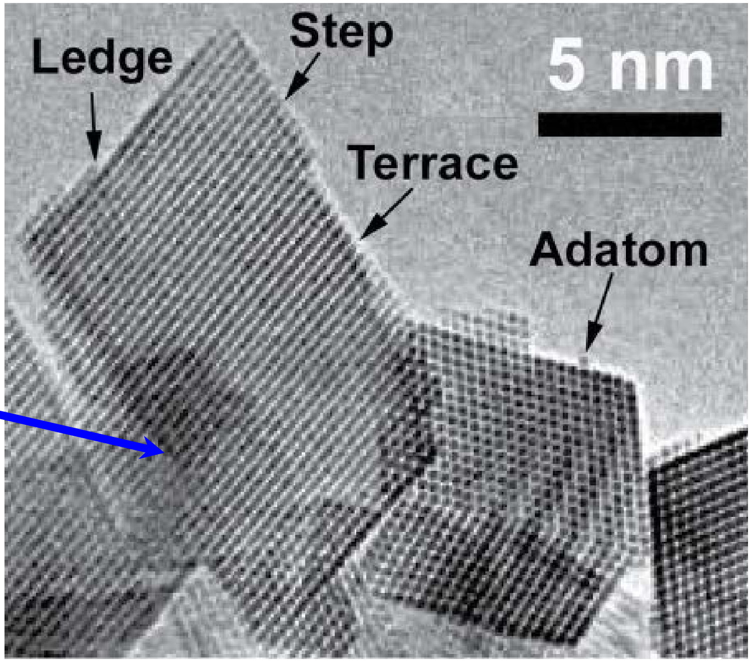


Fig. 6.16, *Callister & Rethwisch 9e.*

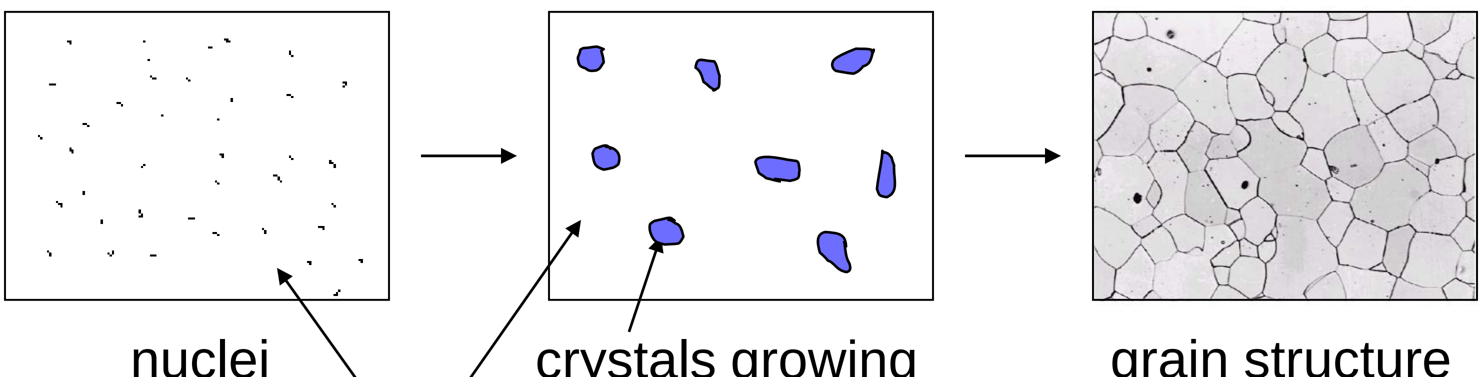


Single crystals of $(Ce_{0.5}Zr_{0.5})O_2$ used in an automotive catalytic converter

Fig. 6.17, *Callister & Rethwisch 9e.*
[From W. J. Stark, L. Mädler, M. Maciejewski, S. E. Pratsinis, and A. Baiker, "Flame Synthesis of Nanocrystalline Ceria/Zirconia: Effect of Carrier Liquid," Chem. Comm., 588–589 (2003). Reproduced by permission of The Royal Society of Chemistry.]

(2) Grain boundaries

- Solidification- result of casting of molten material
  - 2 steps
    - Nuclei form
    - Nuclei grow to form crystals – grain structure
- Start with a molten material – all liquid



Adapted from Fig. 6.20 (b), *Callister & Rethwisch 9e.*

[Photomicrograph 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.)]

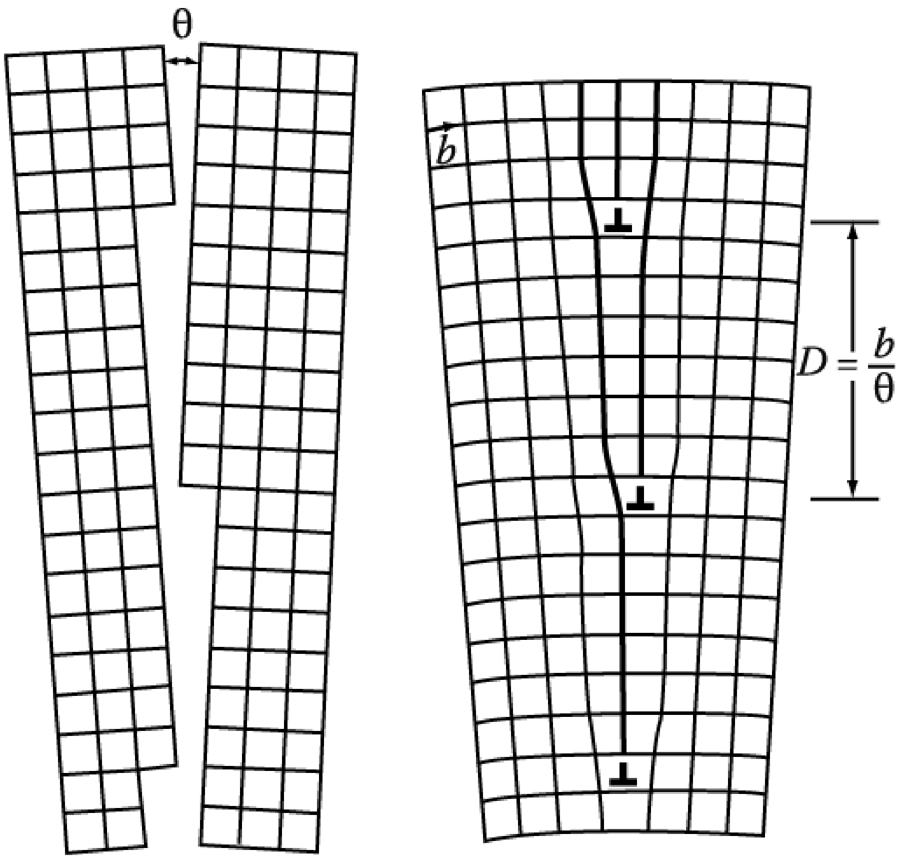
- Crystals grow until they meet each other

3.3.1 Low-Angle and High-Angle Boundaries

Low-Angle Tilt Boundaries

→ **around edge dislocation : strain ↑**

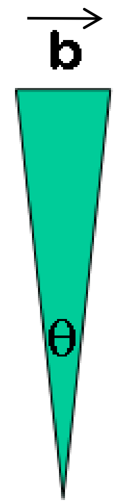
but, LATB ~ almost perfect matching



(a)

→

Burgers vector of the dislocations



Angular mis-orientation across the boundary

$$\sin\frac{\theta}{2} = \frac{\vec{b}/2}{D}$$

$$\sin\frac{\theta}{2} \approx \frac{\theta}{2}$$

$$D \cong \frac{\vec{b}}{\theta}$$

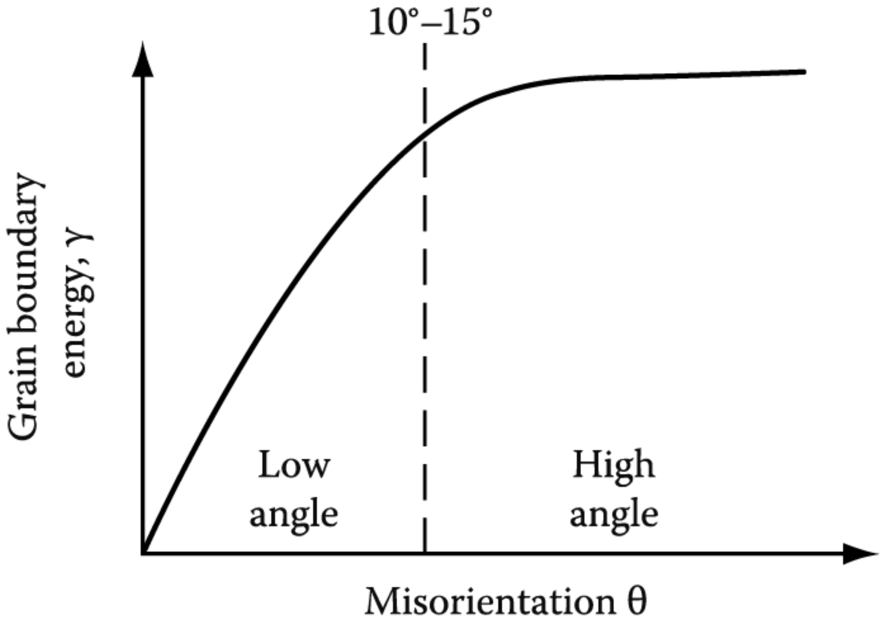
Energy of LATB ~ Total E of the dislocations within unit area of boundary

~ depends on the spacing of the dislocations (D)

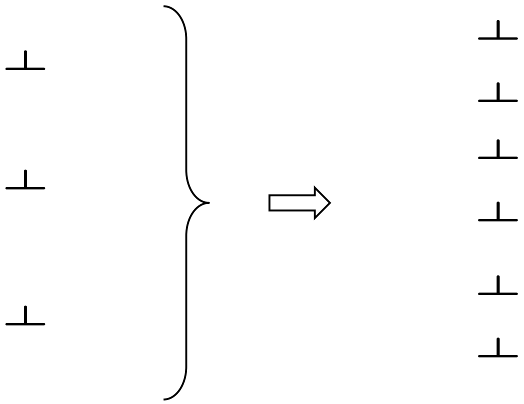
(For brevity, the distinction between internal E and free E will usually not be made from now)

Low-Angle tilt Boundaries

$$\boxed{\gamma \propto \theta}$$



⇨ 1) As θ increases, $\gamma_{g.b.}$ ↑



Strain field overlap

→ cancel out

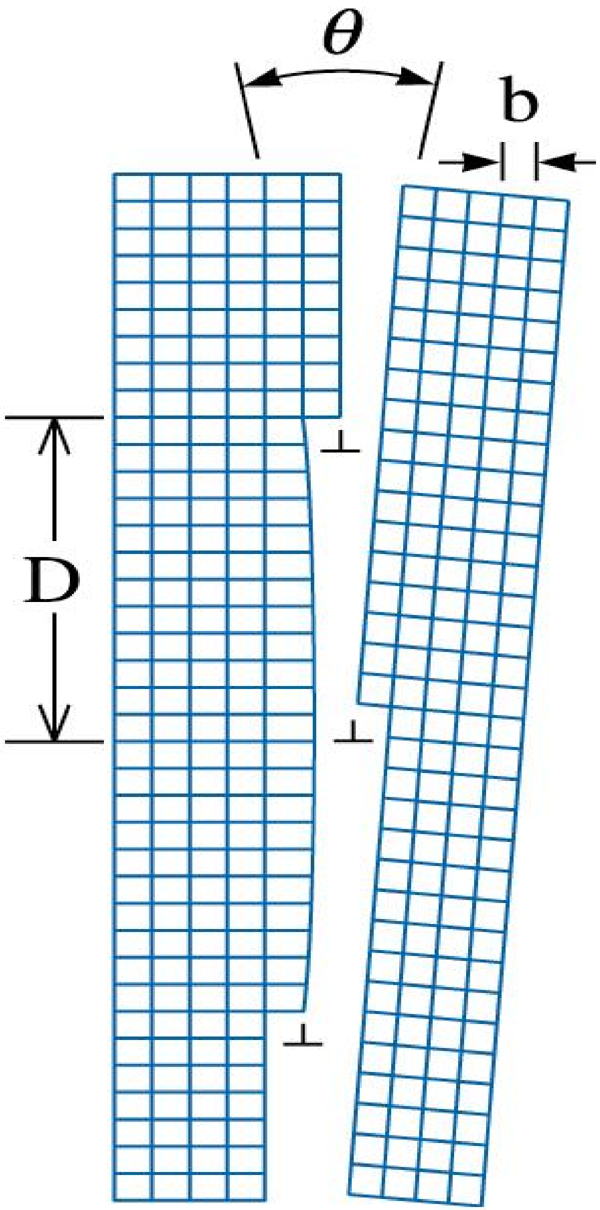
→ **2) $\gamma_{g.b.}$ increases and the increasing rate of γ (=d γ/d θ) decreases.**

→ **3) if θ increases further, it is impossible to physically identify the individual dislocations**

→ **4) When θ > 10°-15°, increasing rate of $\gamma_{g.b.}$ ~ 0**

5) When θ > 10°-15°, Grain-boundary energy ~ almost independent of misorientation

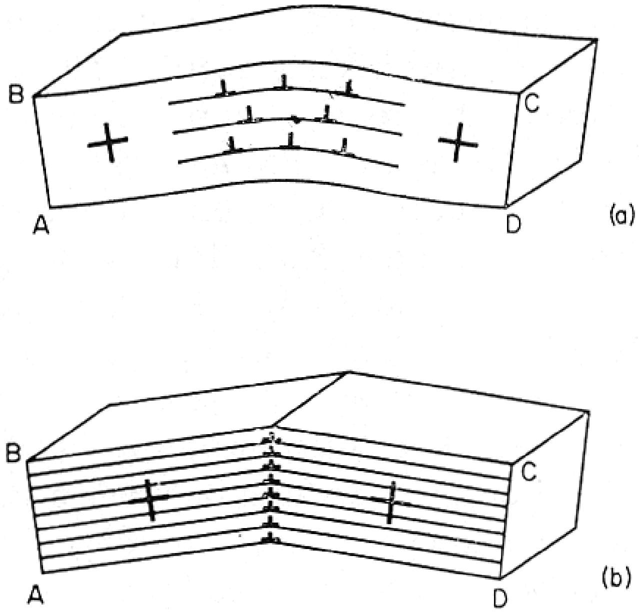
Low Angle Grain Boundary

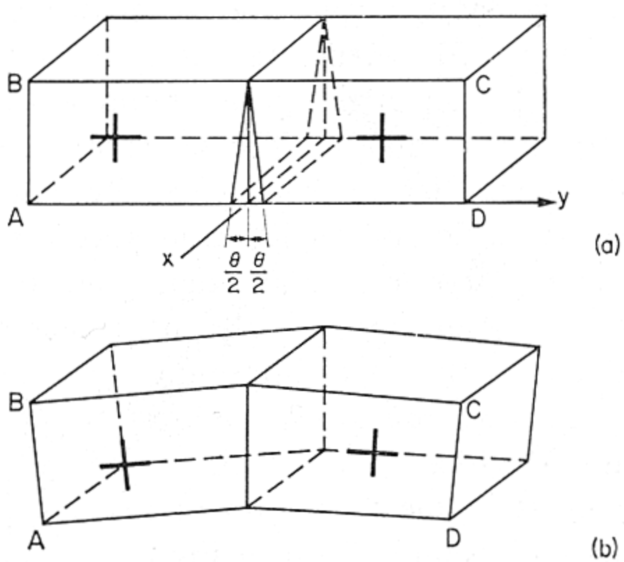


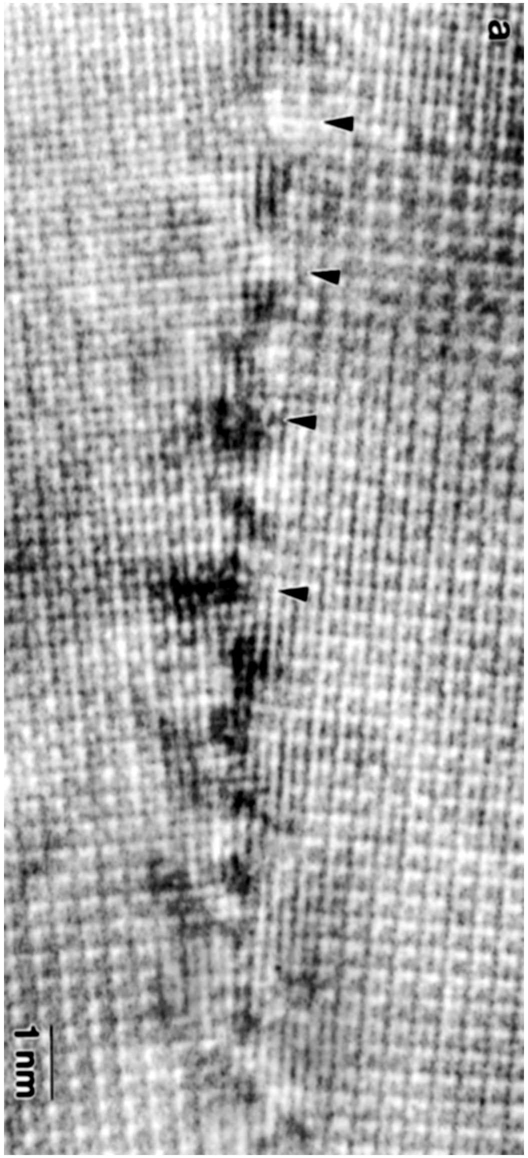
The small angle grain boundary is produced by an array of dislocations, causing an angular mismatch θ between lattices on either side of the boundary.

Concept of Σn boundary

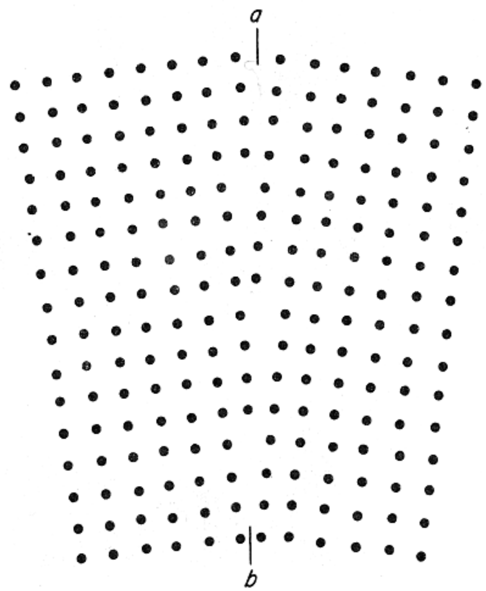
Low angle grain boundaries

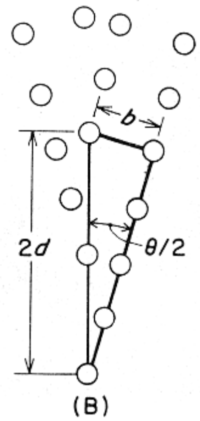






Σ - boundary





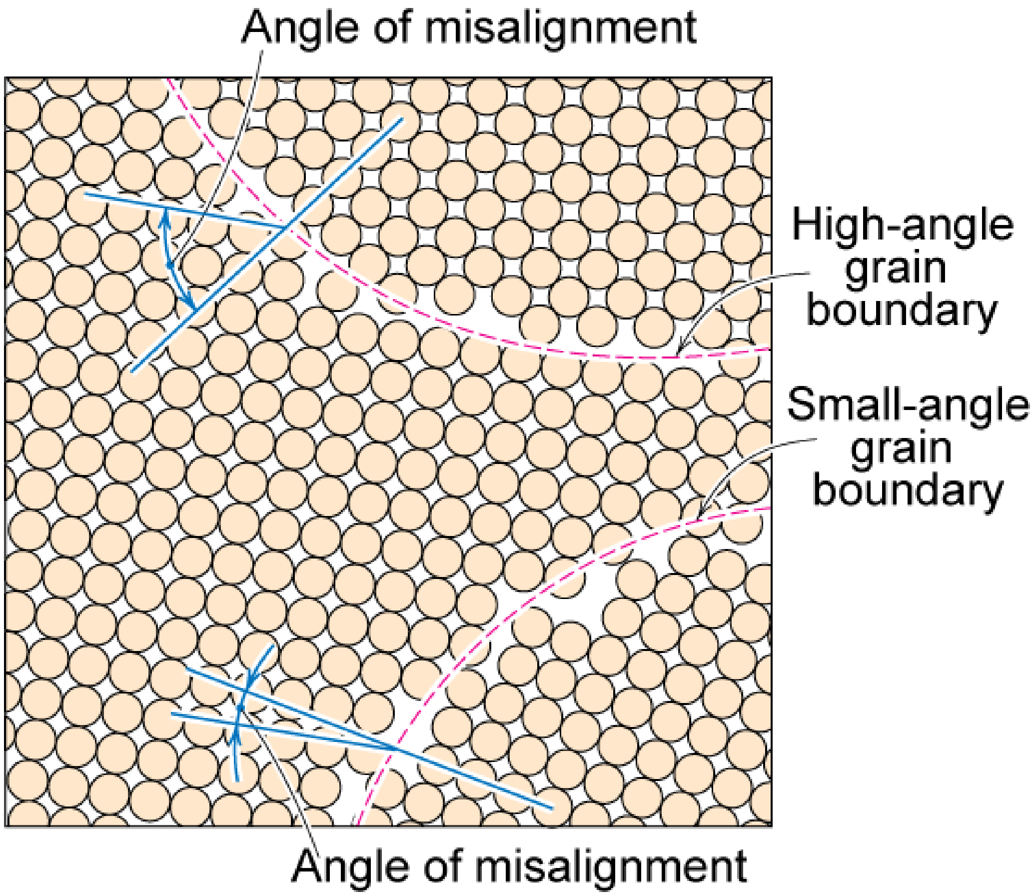
$$\boxed{\theta = \frac{b}{d}}$$

- Low angle boundary : Σ-value is defined as the reciprocal of the ratio of the coincident lattice sites to the original lattice sites.
- Smaller Σ number, better line-up (coincidence)
- Ex. Σ5 boundary : boundaries at an angle θ to each other, i.e. 1/5 coincident in every lattice with θ=36.87°, 53.13°, 126.87°, and 143.13°.

Polycrystalline Materials

Grain Boundaries

- regions between crystals
- transition from lattice of one region to that of the other
- slightly disordered
- low density in grain boundaries
  - high mobility
  - high diffusivity
  - high chemical reactivity



Adapted from Fig. 6.14, *Callister & Rethwisch 9e.*

High Angle Grain Boundary: θ > 10°-15°

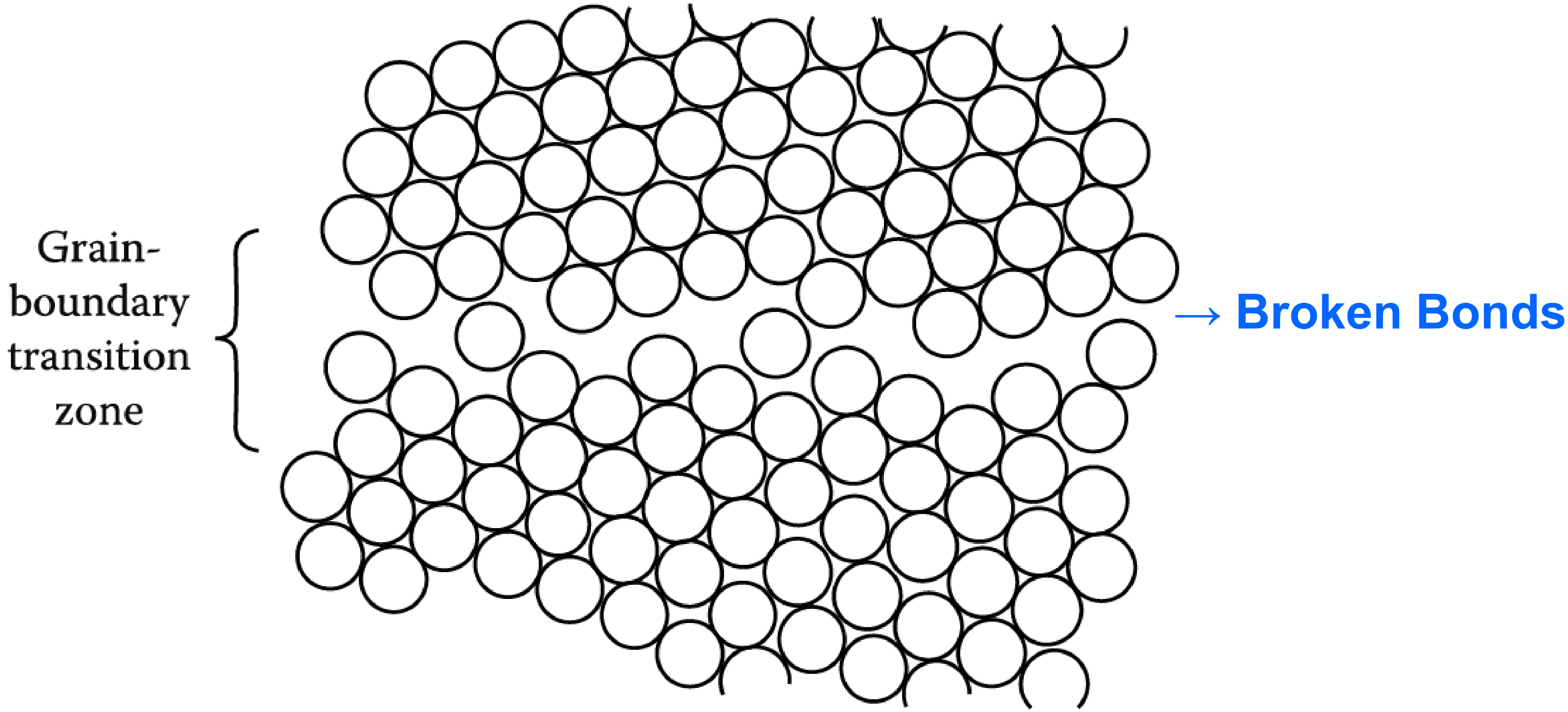


Fig. 3.10 Disordered grain boundary structure (schematic).

High angle boundaries contain large areas of poor fit and have a relatively open structure.

→ high energy, high diffusivity, high mobility **(cf. gb segregation)**

High Angle Grain Boundary

Low angle boundary

→ **almost perfect matching (except dislocation part)**

High angle boundary (almost)

→ **open structure, large free volume**

* low and high angle boundary

high angle $\gamma_{g.b.} \approx 1/3\ \gamma_{S/V.}$ → Broken Bonds

Measured high-angle grain boundary energies

Crystal	γ (mJ m^{-2})	T (°C)	γ_b/γ_{sv}
Sn	164	223	0.24
Al	324	450	0.30
Ag	375	950	0.33
Au	378	1000	0.27
Cu	625	925	0.36
γ-Fe	756	1350	0.40
δ-Fe	468	1450	0.23
Pt	660	1300	0.29
W	1080	2000	0.41

* As for $\gamma_{S/V}$, γ_b is temperature dependent decreasing somewhat with increasing temperature.

Tensile strength of Single crystals

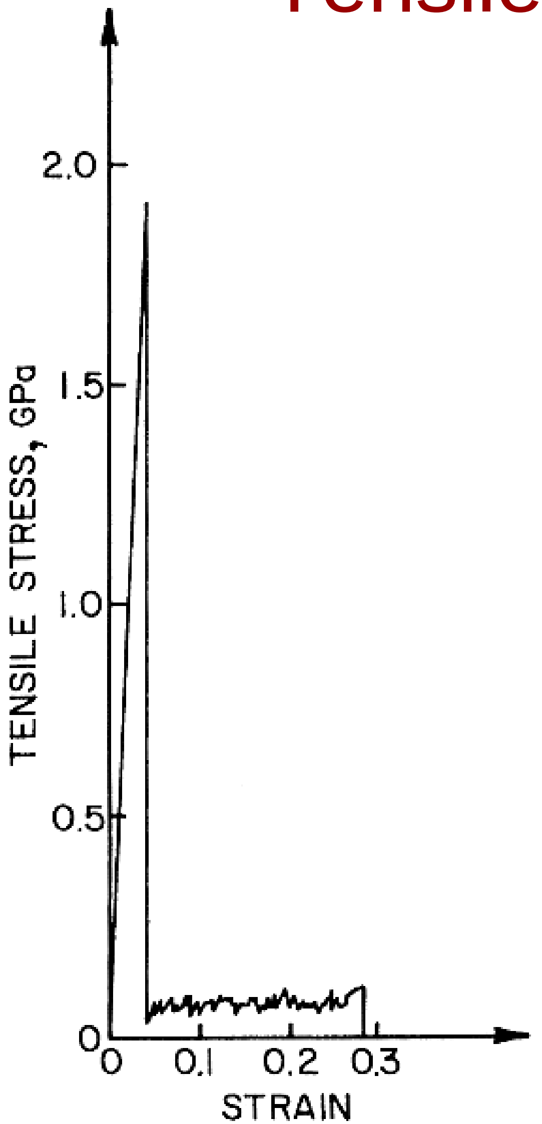


TABLE 1.6 Tensile Strength of Whiskers at Room Temperature*

Material	*Maximum Tensile Strength (GPa)*	*Young's Modulus (GPa)*
Graphite	19.6	686
Al_2O_2	15.4	532
Iron	12.6	196
SiC	20–40	700
Si	7	182
AlN	7	350
Cu	2	192

*Adapted with permission from A. Kelly, *Strong Solids* (Oxford, U.K.: Clarendon Press, 1973), p. 263.

↔ 220 MPa

Ultimate tensile strength of Cu

Figure 1.35 Stress–strain curve of a copper whisker with a fiber direction <100>. The whisker diameter is 6.8 μm. (Adapted with permission from K. Yoshida, Y. Goto, and M. Yamamoto, *J. Phys. Soc. Japan*, 21 (1966) 825.)

- Hall-Petch equation - The relationship between yield strength and grain size in a metallic material — that is $\sigma_y = \sigma_0 + Kd^{-1/2}$

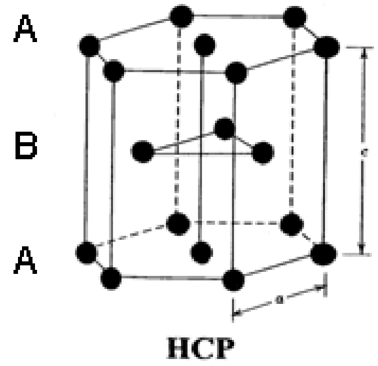
Phase boundary

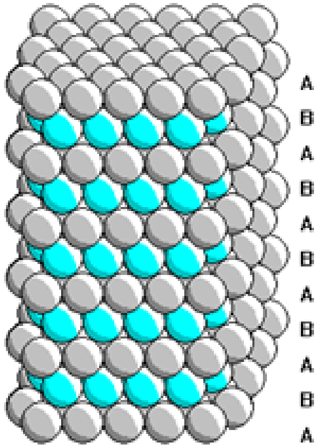
(3) Stacking fault

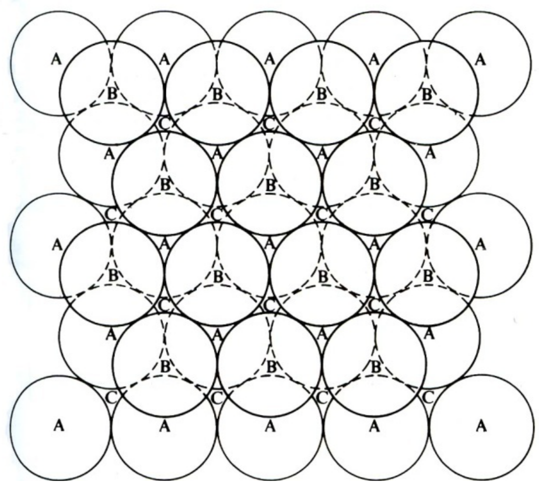
HCP: ABABABAB…

close packed plane: (0001)

close packed directions: $<11\bar{2}0>$



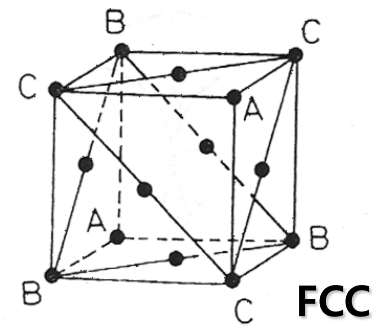


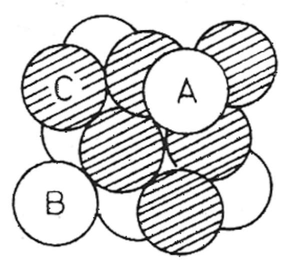


FCC: ABCABCAB…

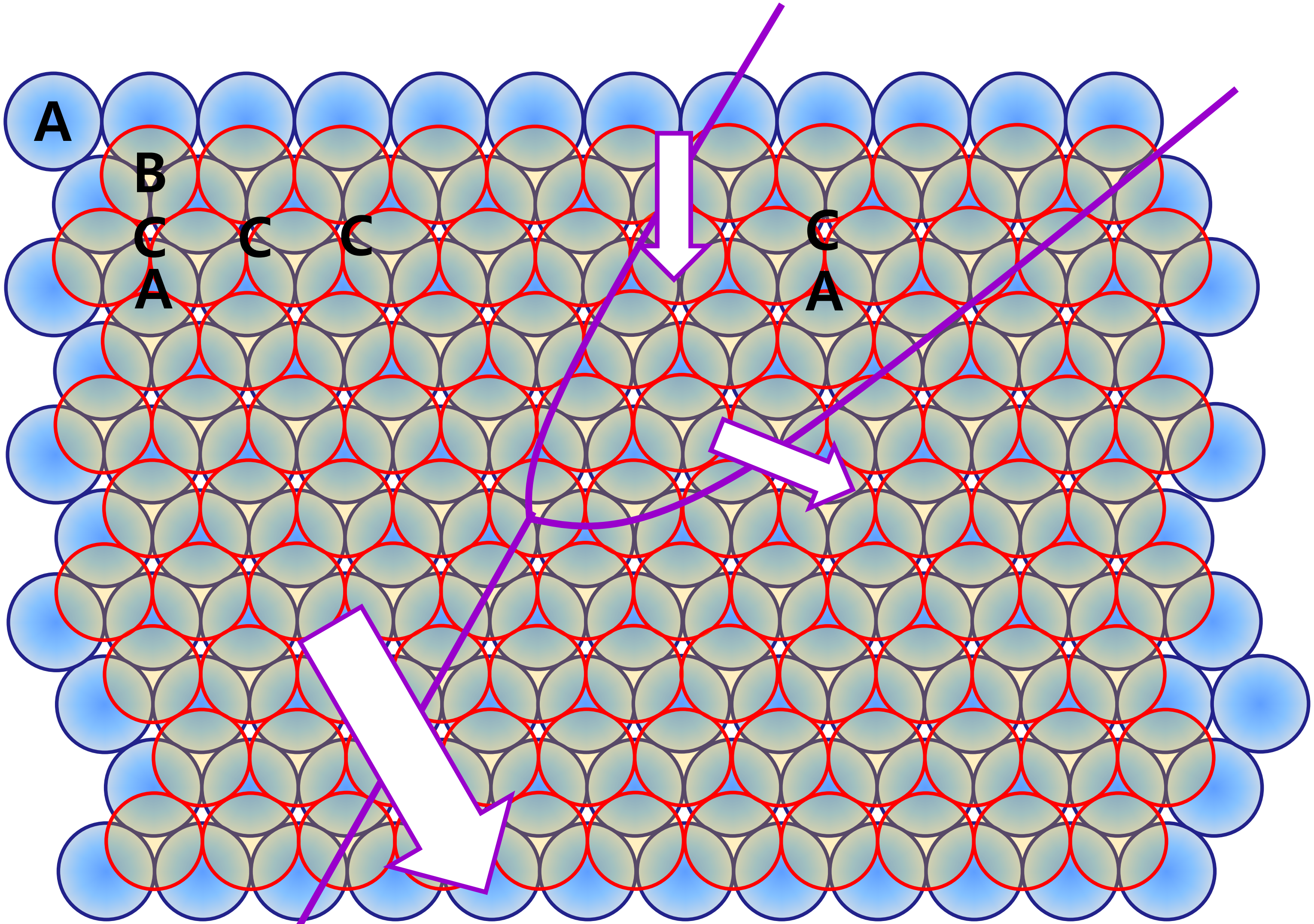
close packed planes: {111}

close packed directions: $<110>$





Two closely packed stackings



From A⇨B ⇨C ⇨A ⇨B to A⇨C ⇨A ⇨B ⇨C

Glissile Interfaces between two lattices

Stacking Faults misfit → hcp

ABCABCABC → $\underbrace{\text{ABCA}}$CABC.........

Sequence of Shorkley partial dislocations between every other (111) plane

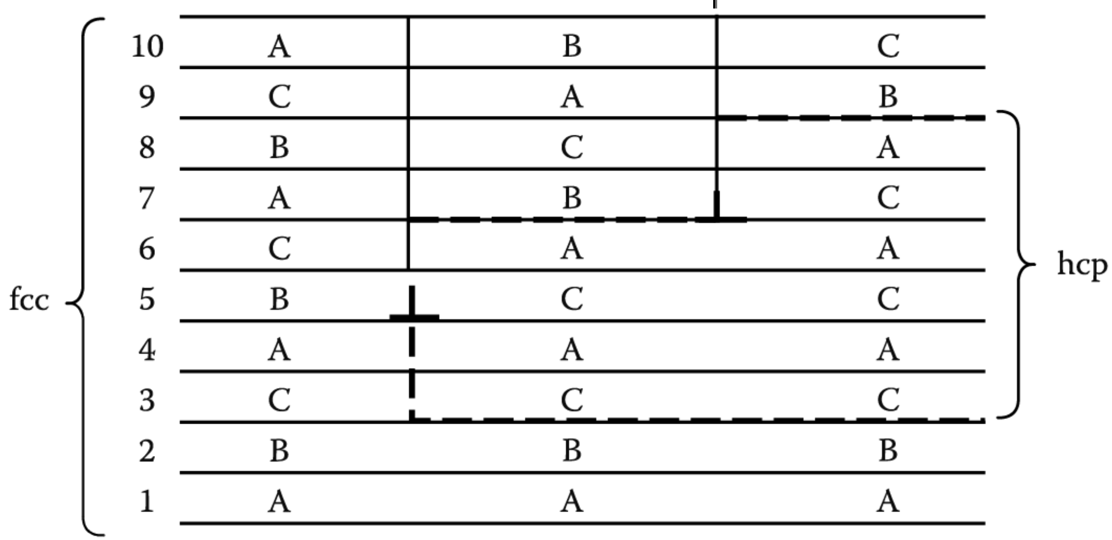
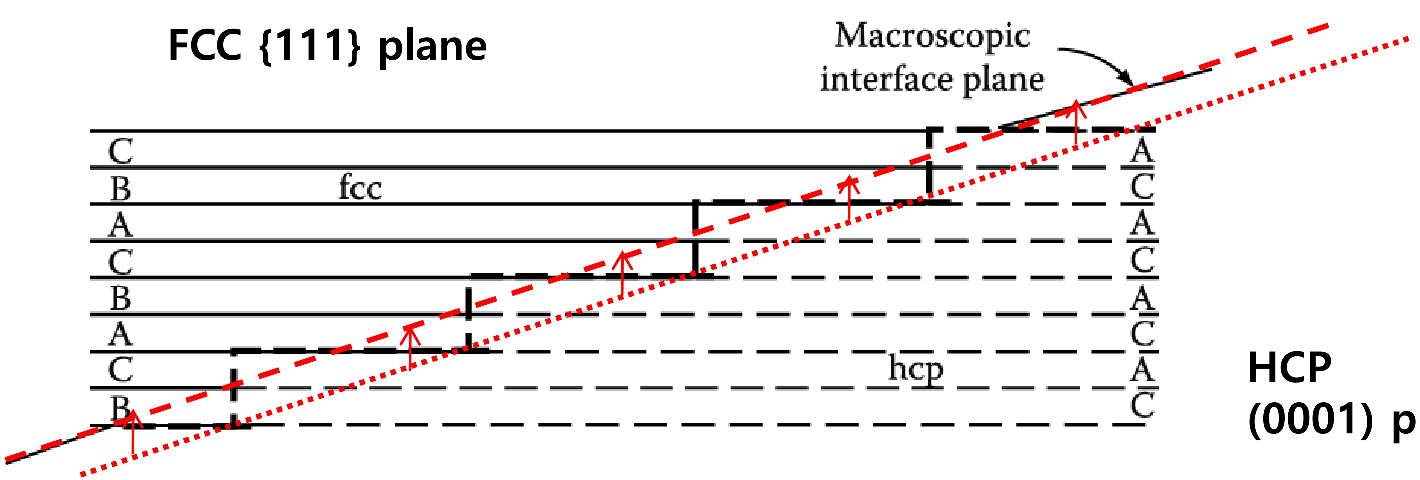


Fig. 3. 60 Two Shockley partial dislocation on alternate (111) planes create six layers of hcp stacking.

FCC {111} plane

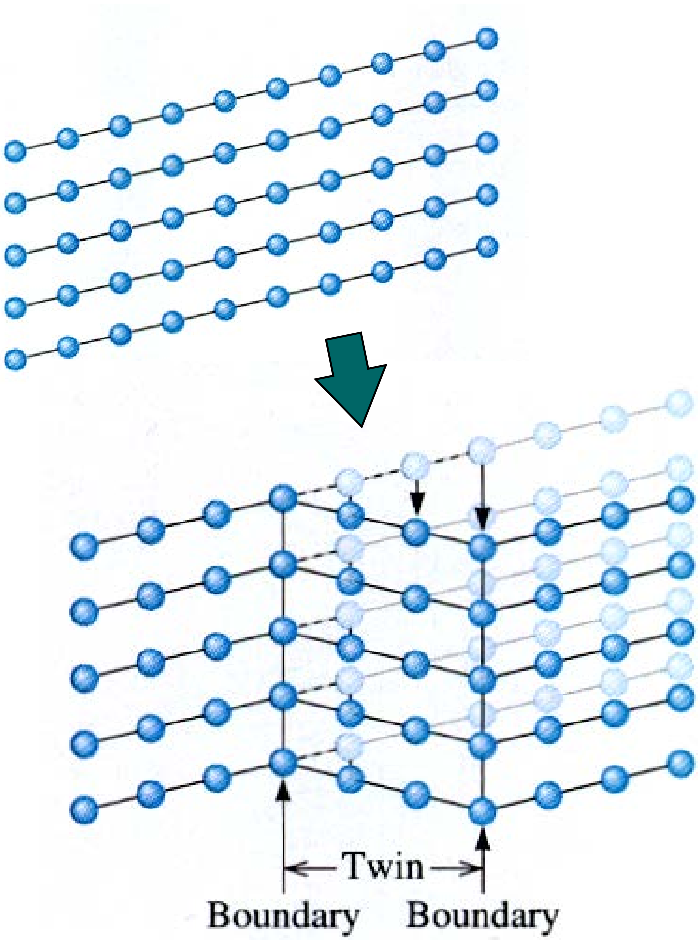


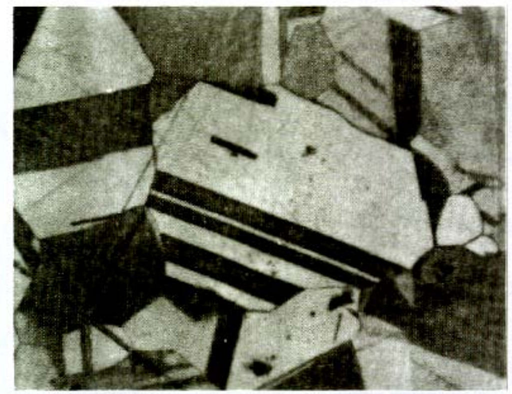
HCP (0001) plane

Fig. 3. 61 An array of Shockley partial dislocations forming a glissile interface between fcc and hcp crystals.

(4) Twin Boundary

- Separates two crystalline regions that are, structurally, mirror images of each other
- Mechanical twins (by deformation), annealing twins (by annealing heat treatment)





Twins within a grain of Brass

TABLE 5.2 Twinning Planes, Directions, and Shears

Structure	*Twin Plane and Direction*	*Shear Strain, γ*
FCC	(111) [112]	0.707
BCC	(112) [111]	0.707
HCP	$(10\bar{1}2)\ [10\bar{1}\bar{1}]$	Cd: 0.171 Zn: 0.139 Mg: 0.129 Ti: 0.139 Be: 0.199

(5) Domain Boundary

- Domain - a small region of the material in which the direction of electric polarization or magnetization remains the same
- ex) ferromagnets (Fe, Co, Ni) ferroelectric (PZT, BaTiO3)

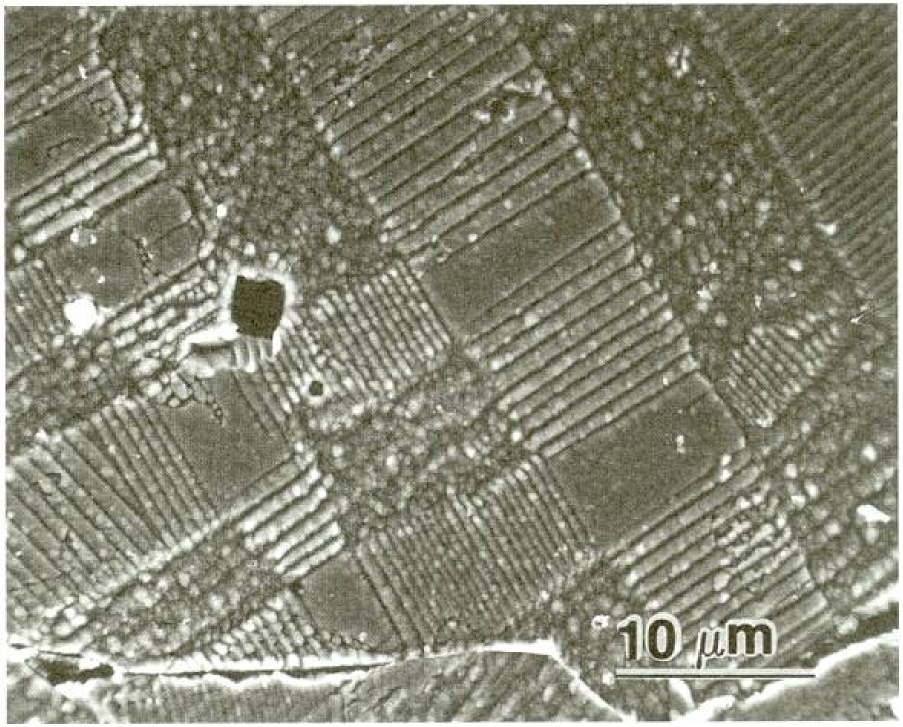


Figure 4-21 Domains in ferroelectric barium titanate. (*Courtesy of Dr. Rodney Roseman, University of Cincinnati.*) Similar domain structures occur in ferromagnetic and ferrimagnetic materials.

IV. Bulk or Volume Defects

(1) Pores

(2) Cracks

(3) Foreign inclusions

(4) Other phases

: normally introduced during processing
  and fabrication steps

V. Microscopic Examination

Microstructure: structure inside a material

that could be observed with the aid of a microscope

Observation of Microstructure: to make image

from the collection of defects in the materials

➡ **OM, SEM, TEM, EXAFS, AFM, SPM**

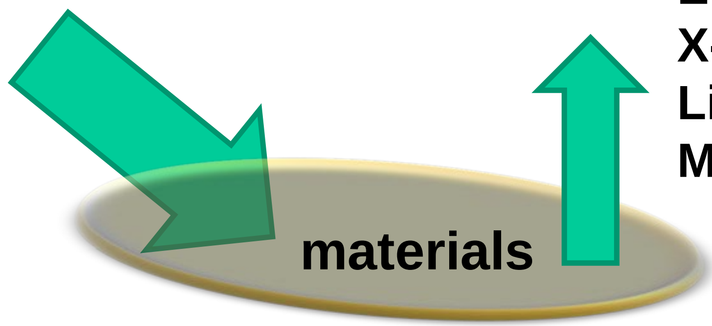
Length Scale of Microstructure

- **Many important intrinsic material properties are determined at the *atomistic length scale*.**

- **The Properties of materials are, how, often strongly affected by the *defect structure*. For example, polycrystals have different properties than single crystals just because of the variation of crystal orientation, combined with the anisotropy of the property. This immediately introduces the idea that the behavior of a material can vary from on location to another.**

Simple idea of analytical tools

Electron
X-ray
Laser
Light
Shockwave
Mechanical



Electron
X-ray
Light
Mechanical

Analytical tool	Abbreviation	Source	Signal	Main Analysis
X-ray diffraction	XRD	X-ray	X-ray	Structure
Transmission Electron Microscopy Scanning Electron Microscopy	TEM SEM	Electron	Electron, Photon (X-ray, Light)	Structure/ Chemistry
X-ray Photoelectron Spectroscopy	XPS	X-ray	Electron	Surface chemistry/ bonding
Auger Electron Spectroscopy	AES	Electron	Electron	Surface chemistry
Energy Dispersive Spectroscopy Wavelength Dispersive Spectroscopy	EDS WDS	Electron	X-ray	Chemistry
Electron BackScattered Diffraction	EBSD	Electron	Electron	Structure/ chemistry

Length Scale of Microstructure

Structure

Nanostructure
0.1-100 nm

Sub-atomic Electronic	Atomic	Microscopic	Bulk
<0.1 nm	0.1-10 nm	1-1000 μm	>1 mm
1 nm = 4×10^{-8} in	HRTEM, STEM SPM (AFM)	Optical Microscope SEM,TEM, XRD	Naked Eye

Optical Microscopy (1)

- Useful up to 2000X magnification
- Polishing removes surface features (e.g., scratches)
- Etching changes reflectance, depending on crystal orientation

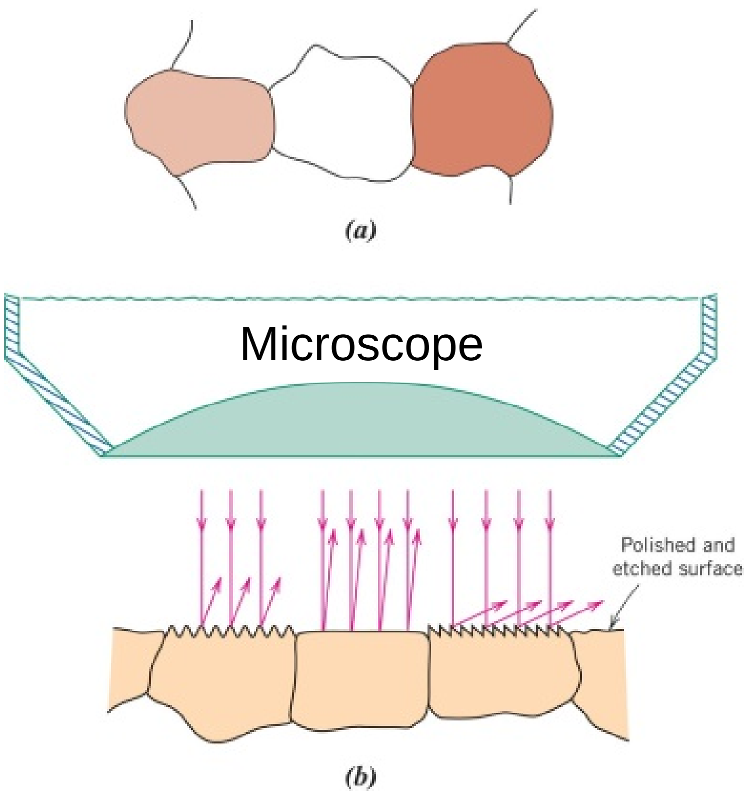
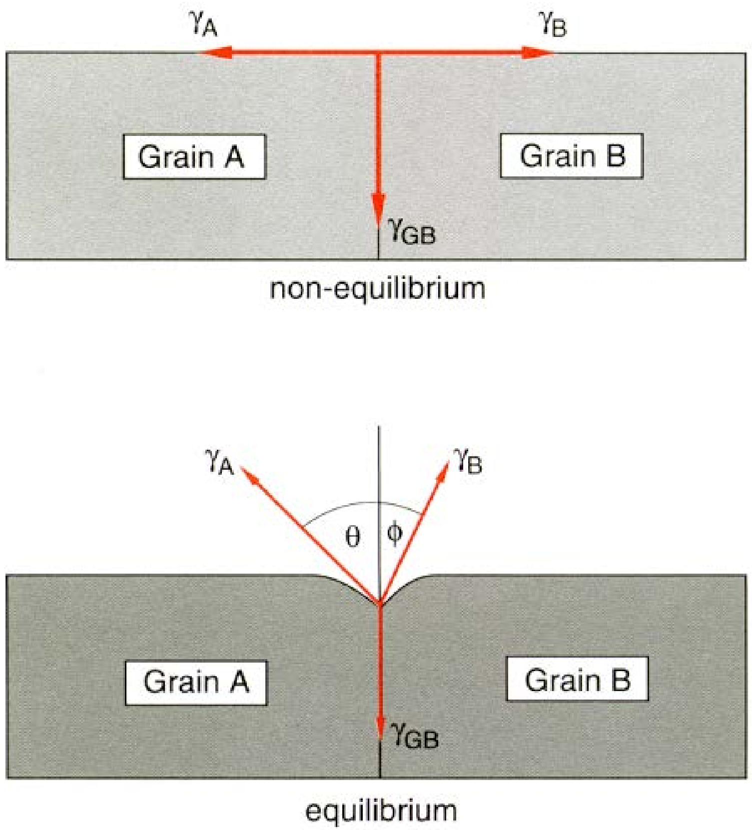


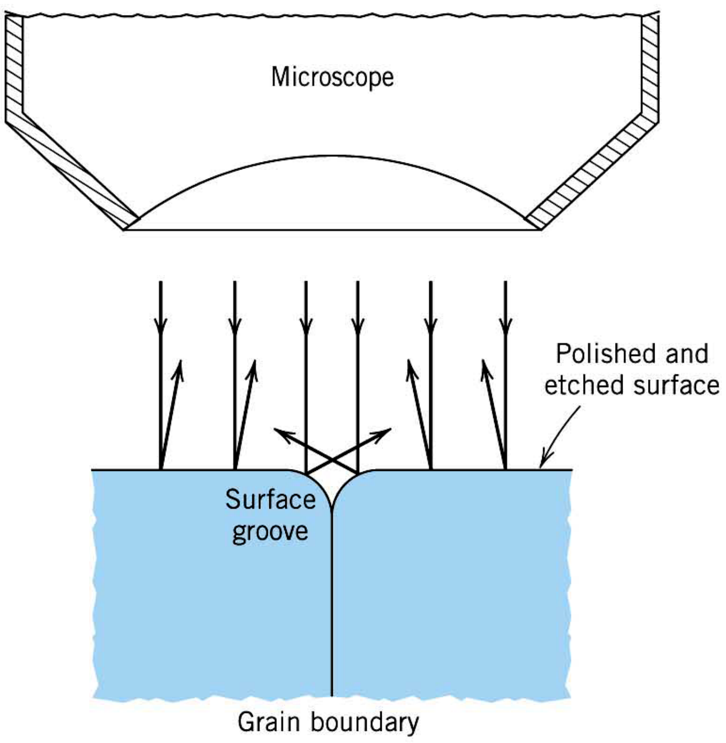
Fig_06_19ab

micrograph of Brass (Cu and Zn)

Observation of Grain Boundary

- Chemical etching
- Thermal etching → groove





* Polarized light

metallographic scopes often use polarized light to increase contrast
Also used for transparent samples such as polymers

Optical Microscopy (2)

- Grain boundaries...
  - ✓ are imperfections
  - ✓ are more susceptible to etching
  - ✓ may be revealed as dark lines
  - ✓ change direction in a polycrystal

ASTM grain size number

$$\boxed{n=2^{G-1}}$$

grains/in² @100X magnification

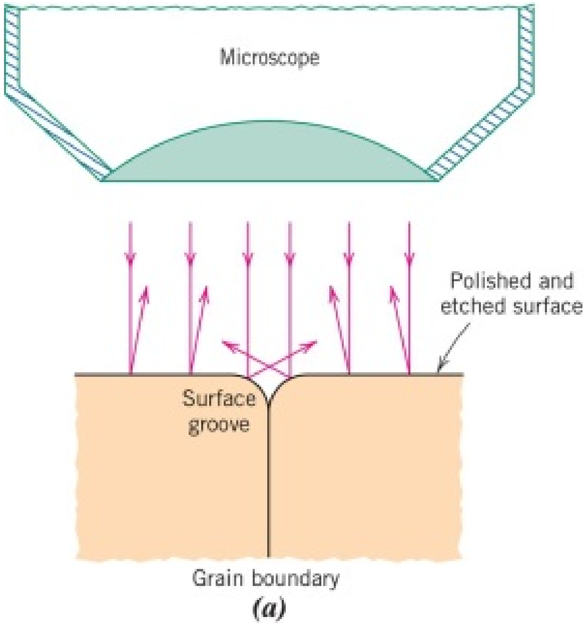


Fig_06_20a

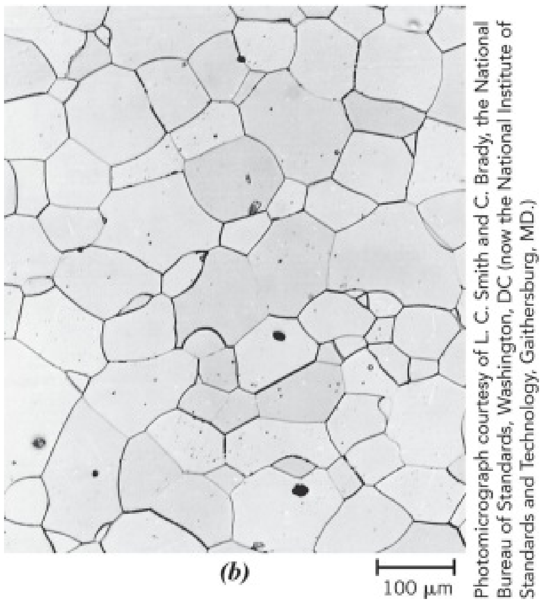
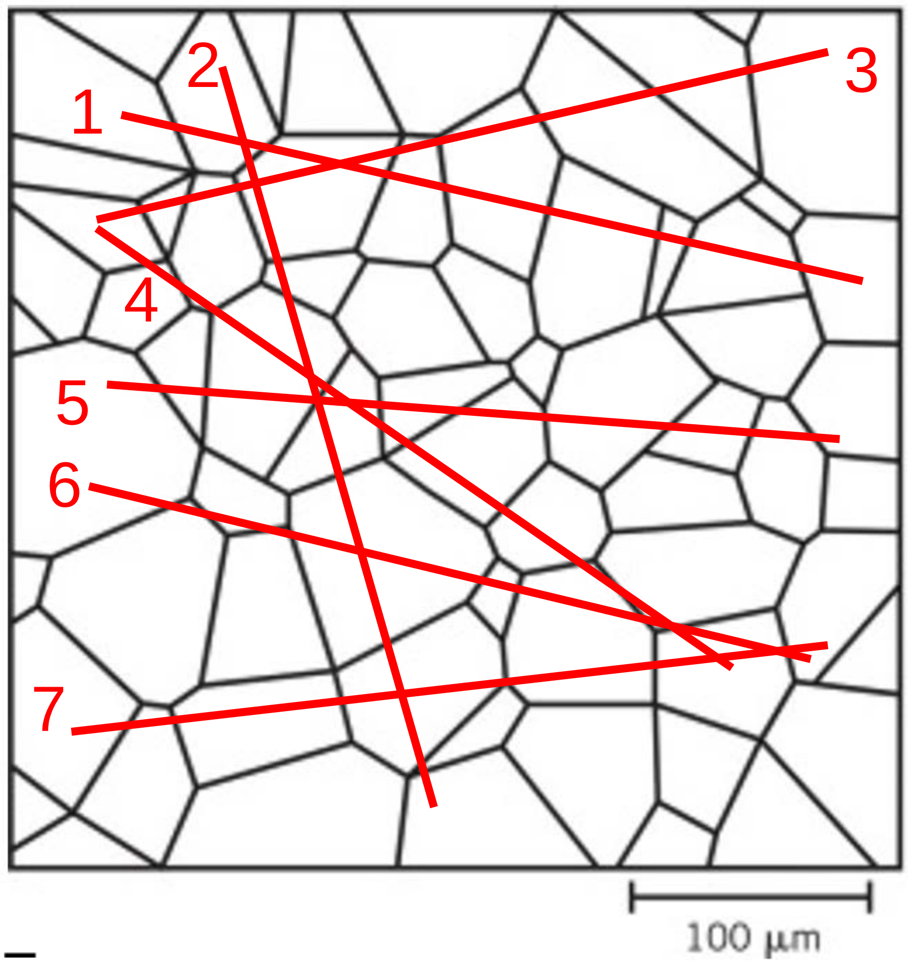


Fig_06_20b

Grain size determination

$$\bar{l} = \frac{L_T}{PM}$$

Line number	# of intersections	
1	8	
2	8	
3	8	
4	9	
5	9	
6	9	
7	9	
Total	58	



$$G = -6.646 log(\bar{l}) - 3.3$$

$\bar{l}$ *in mm*

Measurement of grain number

L_T=350 mm, P=58, and M=160X → 0.0377 mm

$$G = -6.646\log(\bar{l}) - 3.3 = 6.16$$

From exercise 6.7

- If a photo was taken other than 100X magnification,

$$\boxed{n_M\left(\frac{M}{100}\right)^2 = 2^{G-1}}$$

Table 2.7. ASTM Grain Size Numbers

ASTM Grain Size Number *N*	*Average Number of grains per square inch. at 100 X* *n*	*Average Diameter of Grain (Assumed) as sphere at 1 X* *mm*	*Grains per millimeter square at 1 X*
00	1/4	0.51	3.9
0	1/2	0.36	7.8
1	1	0.25	15.5
2	2	0.18	31.0
3	4	0.125	62.0
4	8	0.090	124.0
5	16	0.065	248.0
6	32	0.045	496.0
7	64	0.032	992.0
8	128	0.022	1980.0
9	256	0.016	3970.0
10	512	0.011	7940.0
11	1024	0.008	15870.0
12	2048	0.006	31,700.0

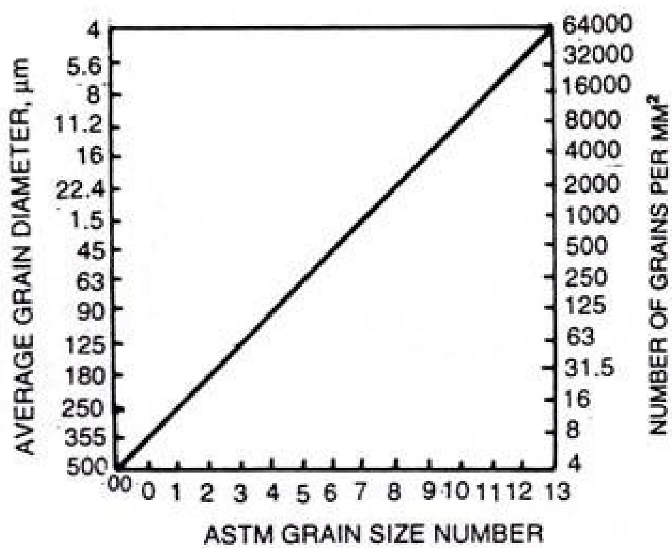


Fig. 2.32. Relationship between ASTM grain size number, average grain diameter and number of grains per mm^2 at 1 X.

Microscopy

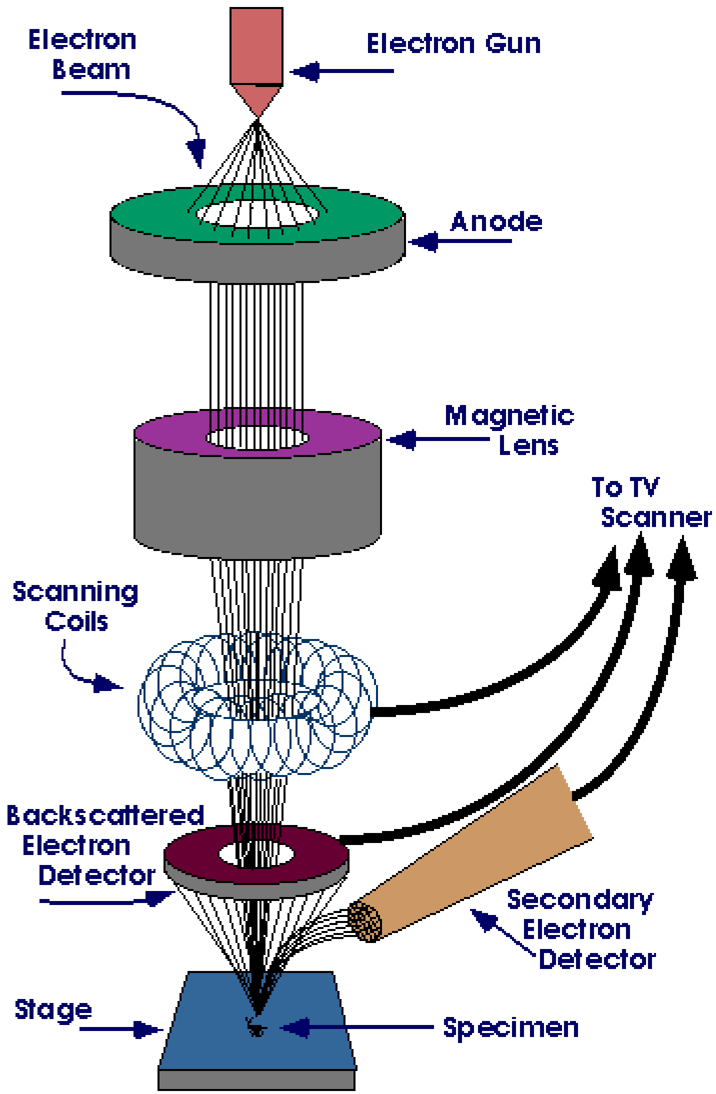
Optical resolution ca. 10^{-7} m = 0.1 μm = 100 nm

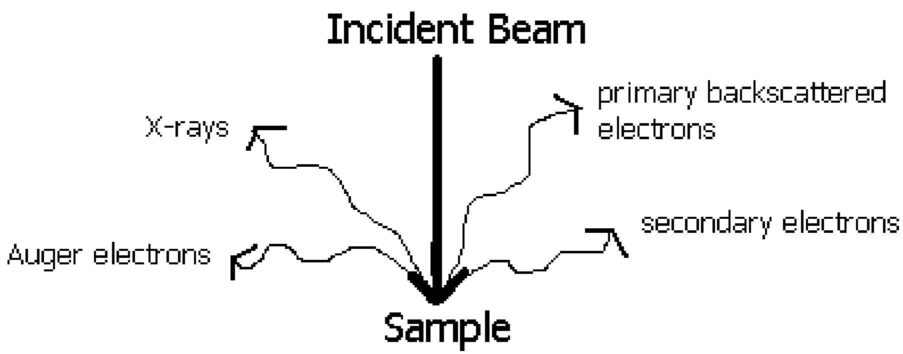
For higher resolution need higher frequency

- X-Rays? Difficult to focus.
- Electrons
  - wavelengths ca. 3 pm (0.003 nm)
    - (Magnification - 1,000,000X)
  - Atomic resolution possible
  - Electron beam focused by magnetic lenses.

SEM (Scanning Electron Microscopy)

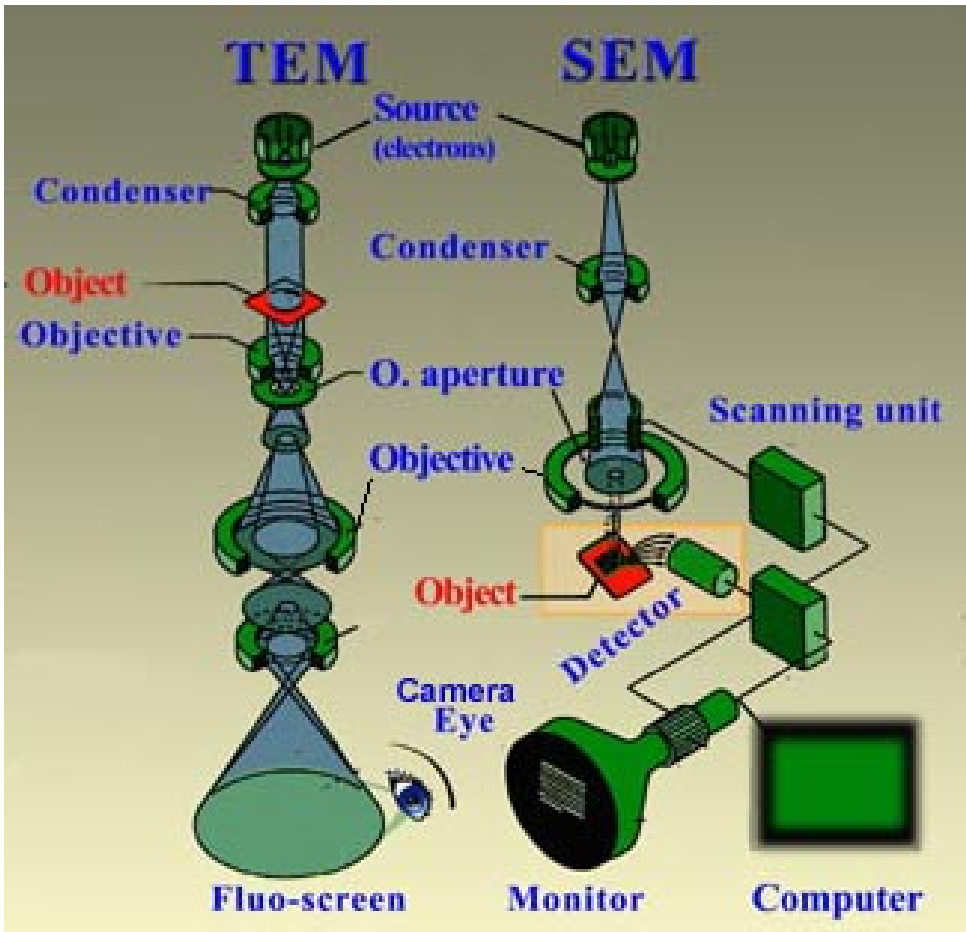
SEM은 Electron beam이 Sample의 표면에 주사하면서 Sample과의 상호작용에 의해 발생된 Secondary Electron를 이용해서 Sample의 표면을 관찰하는 장비이다.





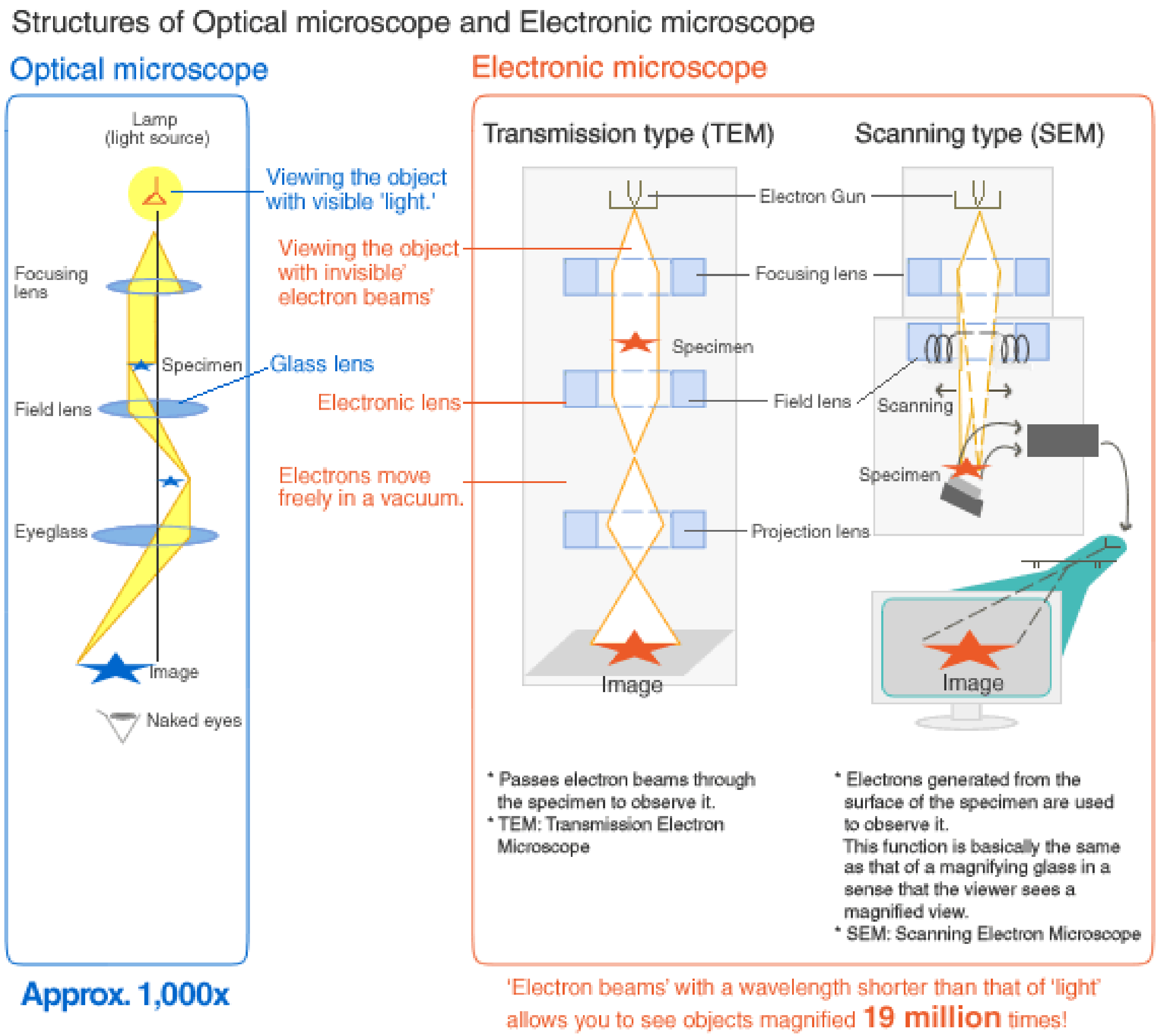
TEM (Transmission Electron Microscopy)

TEM은 electron beam이 통과할 수 있도록 ultrathin sections을 만들어 관찰할 수 있도록 하는 기능적 장치로 여러 가지 각각의 시스템으로 구성되어 있다.



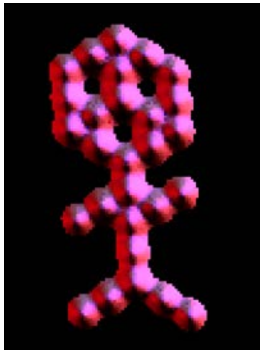
Optical Microscope

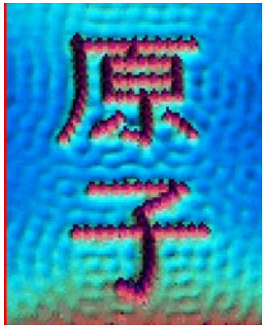
OM과 TEM은 기본적인 구성 즉 렌즈의 배열은 같으나 렌즈를 무엇을 사용하느냐 하는 차이 이다. OM은 유리(glass)를 EM은 magnetic lens를 사용한다. 광원은 OM이 시광을 EM이 전자(빔)를 사용하므로 전자현미경은 칼라 상을 볼 수 없는 것이다.



Scanning Tunneling Microscopy (STM)

- Atoms can be arranged and imaged!





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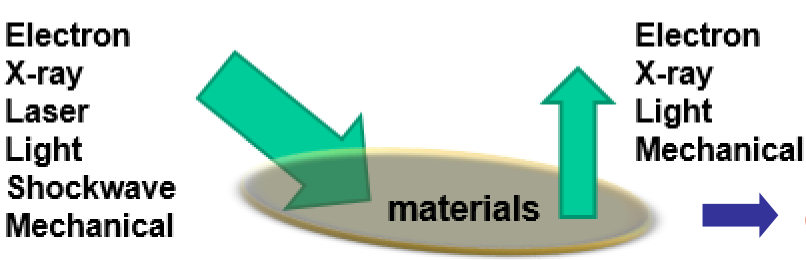
Carbon monoxide molecules arranged on a platinum (111) surface.

Iron atoms arranged on a copper (111) surface. These Kanji characters represent the word “atom”.

Summary

- Point, Line, Area and Volume defects exist in solids.
- The number and type of defects can be varied and controlled (e.g., temperature controls vacancy concentration).
- Defects affect material properties (e.g., grain boundaries control crystal slip).
- Defects may be desirable or undesirable (e.g., dislocations may be good or bad, depending on whether plastic deformation is desirable or not).
- Observation of Microstructure: to make image from the collection of defects in the materials



OM, SEM, TEM, EXAFS, AFM, SPM