Chapter 5: Imperfections in Solids

ISSUES TO ADDRESS...

- What types of **defects** exist in solid materials?
- How does the number of vacancies depend on **temperature**?
- What are the **two types of solid solutions**?
- What are the **three types of dislocations**?
- What kinds of information come from microscopic examinations?

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Imperfections in Solids

There is no such thing as a perfect crystal.

Crystalline imperfections (or defects) are always present.

- Many of the properties of materials are sensitive to the presence of imperfections.
- Crystalline defect 缺陷 refers to a lattice 格子 irregularity with dimensions 尺寸 on the order of an atomic diameter.
- What kinds of crystalline imperfections exist in solids?

Types of Imperfections

- Vacancies（空位）
- Interstitial atoms（填充）
- Substitutional impurity atoms（取代）

Point defects (0-Dimensional)

- Dislocations

Linear defects (1-Dimensional)

- Grain Boundaries
  晶粒邊界

Interfacial defects (2-Dimensional)

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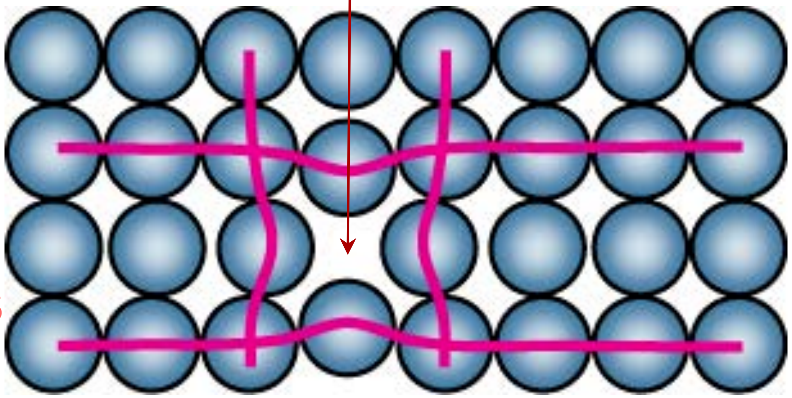
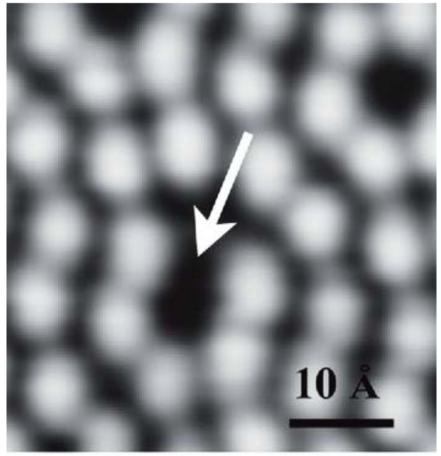
Point Defects in Metals

- **Vacancies(空位):**

  -Vacant atomic sites.

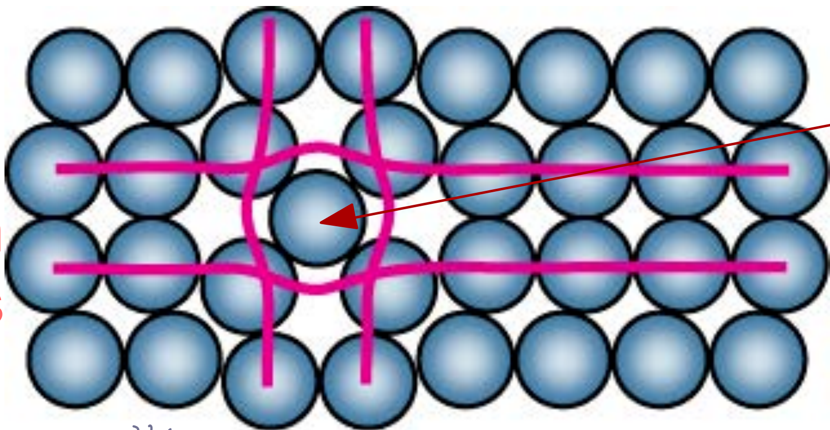




Micrograph courtesy of D. Huang, Stanford University.

- **Self-Interstitials(自填隙):**

  -Host atoms positioned in interstitial positions between atoms.



原子大→形變大

Vacancies –

Computation of Equilibrium Concentration

平衡濃度

- Equilibrium concentration varies with **temperature**!

空洞
洞

Nv
空洞平衡數

Equilibrium number of vacancies

Energy required for the formation of vacancy (Activaton energy)

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

Total number of lattice sites

Boltzmann's constant

Absolute Temperature ($^{o}K = {}^{o}C + 273.15$)

(1.38×10^{-23} J/atom-K)

(8.62×10^{-5} eV/atom-K)

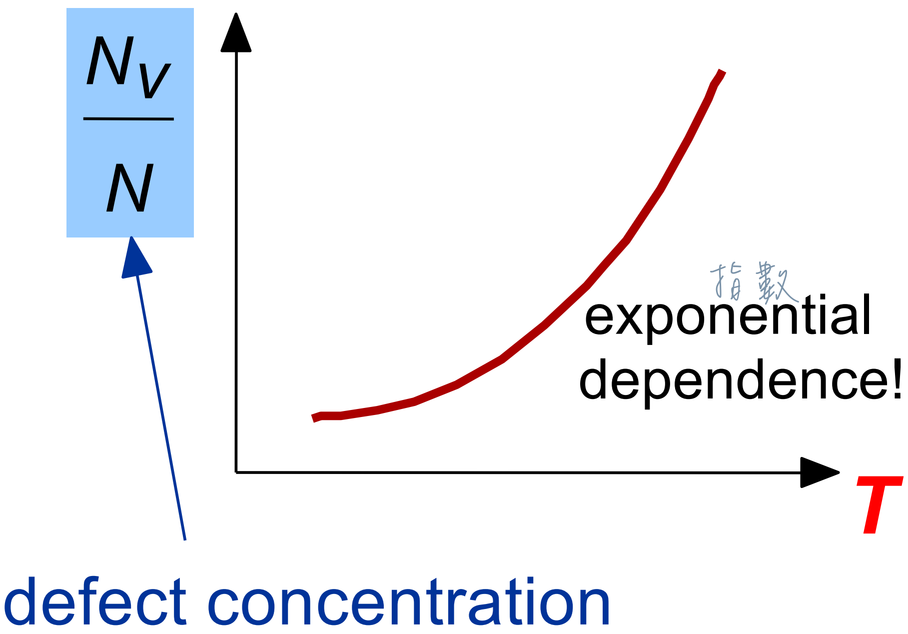
Note: Each lattice site is a potential vacancy.

Determination of Activation Energy for Vacancy Formation

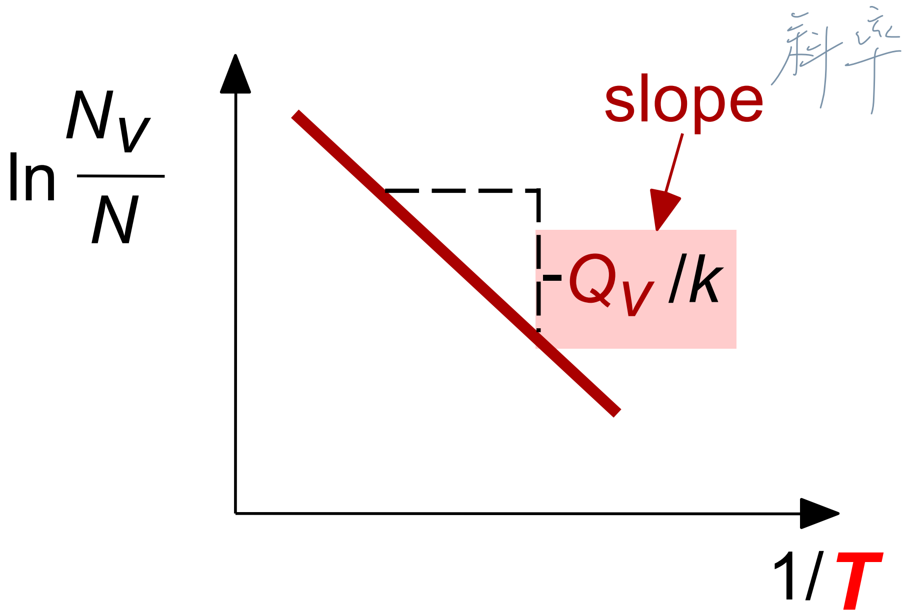
- Q_v can be determined experimentally.

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

- Data may be plotted as...



- Replot data as follows...



Computation of Equilibrium Vacancy Concentration

- Find the equilibrium number of vacancies (N*v*) in

  1 m^3 of **Cu** at 1000 °C

  1273 °K

- Given:

  $\frac{A}{體} = \rho$ → mol/cm^3

  ρ = 8.4 g/cm^3 A_{Cu} = 63.5 g/mol

  Q_V = 0.9 eV/atom N_A = 6.022 x 10^{23} atoms/mol

Solution:

1st: Determine the total number of lattice sites N using Equation 4.2

Number of atoms per unit volume for a metal

$$\boxed{N_{Cu} = \frac{N_A \rho}{A_{Cu}}} = \frac{(6.022 \times 10^{23} \text{ sites/mol})(8.4 \text{ g/cm}^3)}{63.5 \text{ g/mol}} \left(\frac{10^6 \text{cm}^3}{\text{m}^3} \right)$$

= 8.0 x 10^{28} sites/m^3

Computation of Equilibrium Vacancy Concentration

2nd : determine the equilibrium vacancy concentration N_V using Equation 4.1.

$$N_V = N \exp\left(\frac{-Q_V}{kT}\right) = N \exp\left(\frac{-0.9 \text{ eV/atom}}{(8.62 \times 10^{-5} \text{ eV/atom-K})(1273 \text{ K})}\right)$$

$$= (2.7 \times 10^{-4})\, N$$

mol

$$N_v = \frac{N_A \rho}{A} \exp\left[\frac{-Q_V}{kT}\right]$$

- Answer:

$$N_V = (2.7 \times 10^{-4})(8.0 \times 10^{28}) \text{ sites/m}^3$$

$$= 2.2 \times 10^{25} \text{ vacancies/m}^3$$

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Point Defects in Ceramics

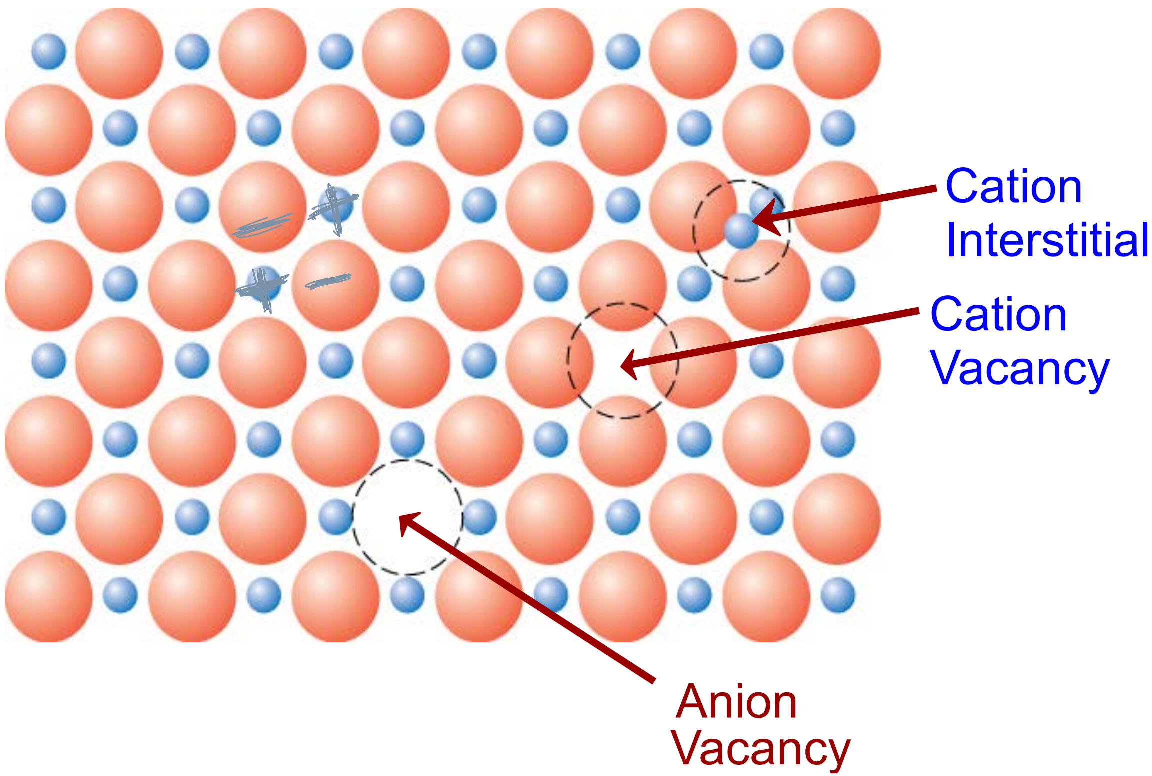
- **Vacancies**

  -- vacancies exist in ceramics for both cations and anions

- **Interstitials** 間隙

  -- interstitials exist for **cations** 陽

  -- interstitials are not normally observed for anions because anions are large relative to the interstitial sites



缺：⊕、⊖
隙：⊕（∵⊖大）

Fig. 5.2, *Callister & Rethwisch 5e.* (Fig. 5.2 is from W.G. Moffatt, G.W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. 1, *Structure*, John Wiley and Sons, Inc., p. 78.)

Point Defects in Ceramics

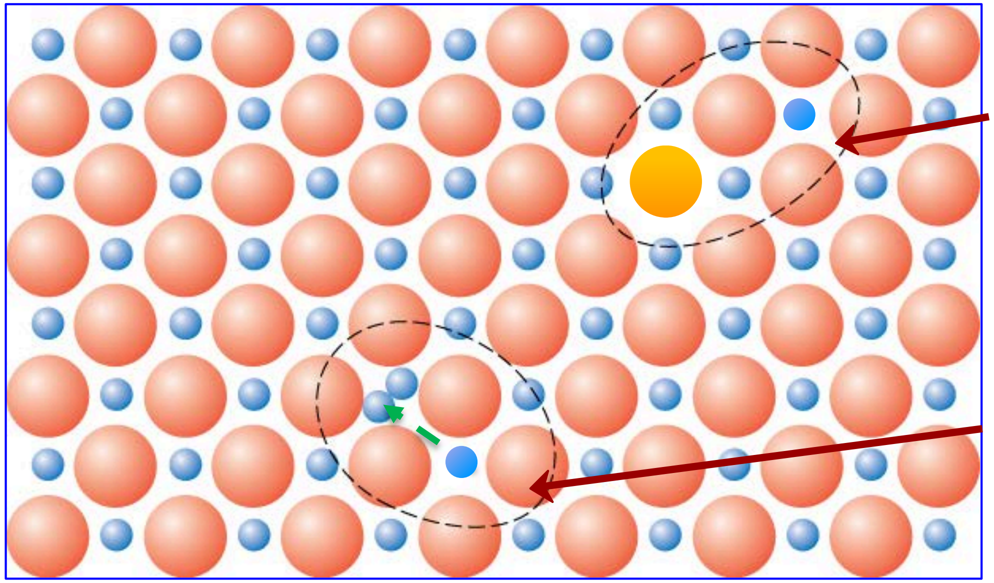
- Frenkel Defect

  -- a cation vacancy-cation interstitial pair.

Schottky

- ~~Shottky~~ Defect

  -- **a paired set** of cation and anion vacancies.



Shottky Defect:

AX materials

Frenkel Defect

- Equilibrium concentration f defects $\propto e^{-Q_D/kT}$

Point Defects in Ceramics

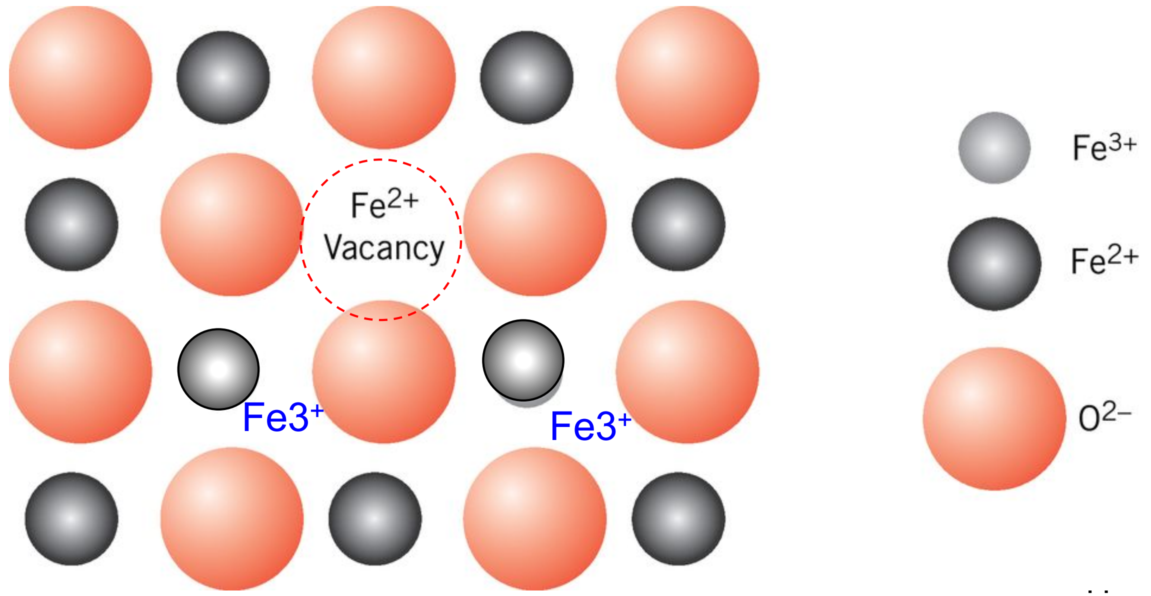
Iron oxide (FeO) Fe^{2+} O^{2-}

- Fe^{2+} or Fe^{3+}

溫度 周遭氧氣壓力

- The formation of ions depends on temperature and the ambient oxygen pressure.
- **Fe^{3+} ion disrupts the electron neutrality** of the crystal by introducing a **excess +1 charge**, which must be offset by some type of defect.
- Accomplished by the formation of one Fe^{2+} vacancy (*or removal of two positive charges*) for every two Fe^{3+} ions that are formed.

$Fe_{1-x}O$



Impurities in Solids

in Metals

代用的

Conditions for formation of substitutional solid solutions

W. Hume – Rothery rules

半徑差

– 1. **Δ*r* (atomic radius)** < 15%

– 2. **Proximity in periodic table** 元素週期表中的鄰近程度

- i.e., similar **electronegativities**

晶格結構

– 3. **Same crystal structure** for pure metals

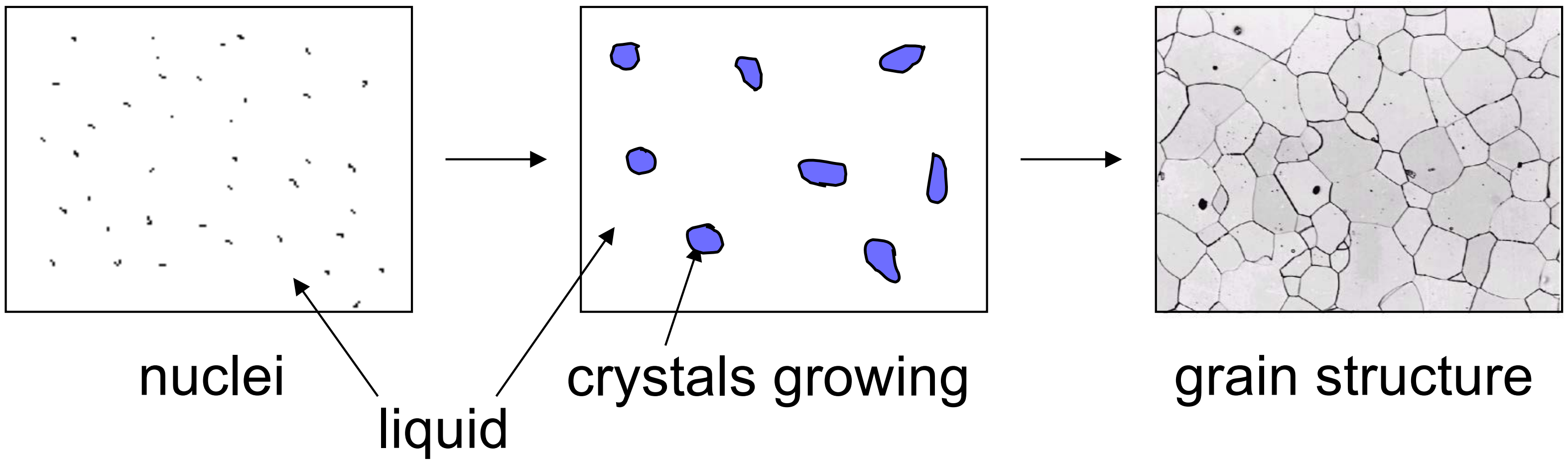
– 4. **Valences** 價電子(價數)

- All else being equal, a metal will have a greater tendency to dissolve a metal of higher valence than one of lower valence

Solidification

- **Solidification**- result of casting of molten material
  - 2 steps
    固相核
    - **Nuclei** of the solid phase form
    - **Crystals grow** until their boundaries meet each other – the crystals become grains
    結晶

- Start with a molten material – all liquid



[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.)]

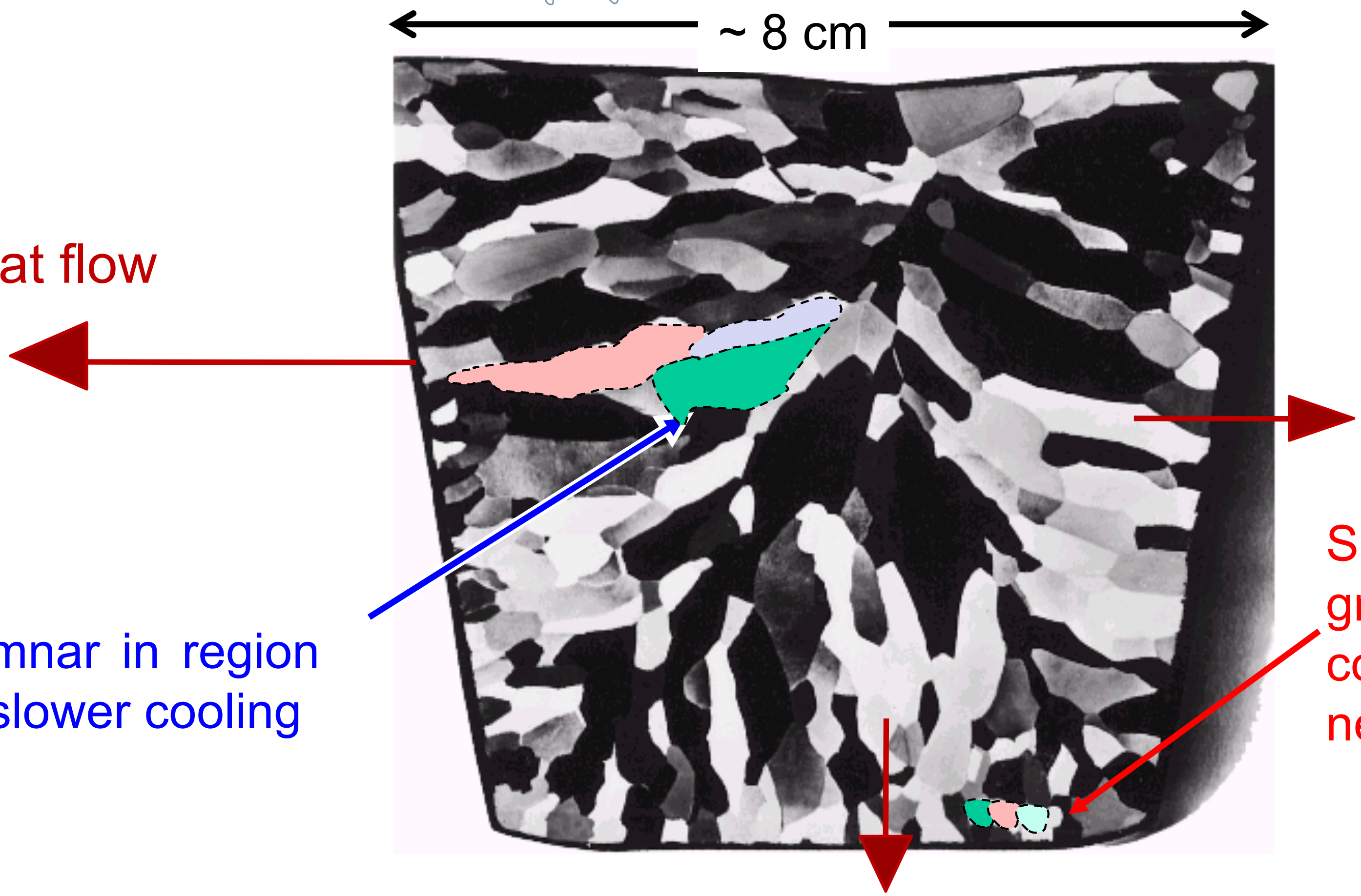
- Two metal element –alloy   minor: solute;   major: solvent

合金

Solidification

Grains can be - **equiaxed** (roughly the same dimension in all directions)
等大 尺寸

- **columnar** (grains elongated in one direction)
等向



Reproduced with permission from Metals Handbook, Vol. 9, 9th edition, Metallography and Microstructures, ASM International, Materials Park, OH, 1985.

Heat flow

Columnar in region with slower cooling

Shell of equiaxed grains due to rapid cooling (greater ΔT) near wall

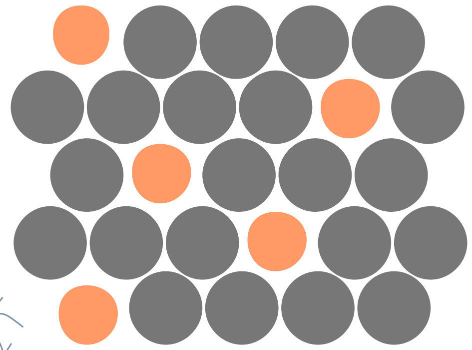
Grain Refiner - added to make smaller, more uniform, equiaxed grains.

Impurities in Solids

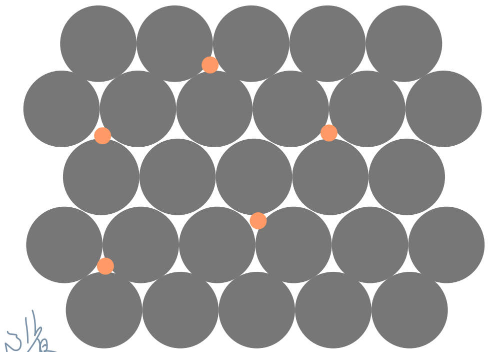
in Metals

Two outcomes if impurity **B** atoms are added to a solid composed of host A atoms:

- Solid solution of **B** in A (i.e., random dist. of B atoms)



OR



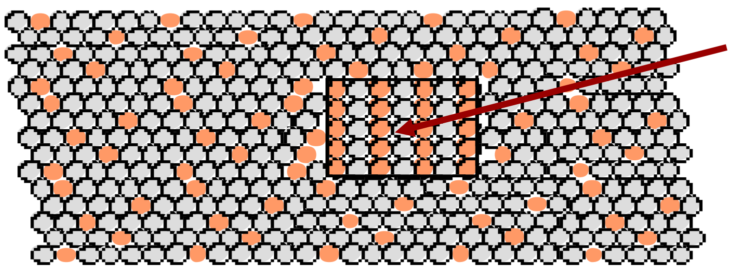
替

Substitutional solid soln.
(e.g., Cu in Ni)

隙

Interstitial solid soln.
(e.g., C in Fe)

- Solid solution of B in A, plus particles of a new phase
  (usually for larger concentrations of B)



Second phase particle

-- different composition

-- often different structure.

5.4 Impurities in Solids

in Metals

Application of Hume–Rothery rules – Solid Solutions

Ex: Would you predict more Al or Ag to dissolve in Zn?

Element	*Atomic Radius (nm)*	*Crystal Structure*	*Electro-nega-tivity*	*Valence*
Cu	0.1278	FCC	1.9	+2
C	0.071			
H	0.046			
O	0.060			
Ag	0.1445	FCC	1.9	+1
Al	0.1431	FCC	1.5	+3
Co	0.1253	HCP	1.8	+2
Cr	0.1249	BCC	1.6	+3
Fe	0.1241	BCC	1.8	+2
Ni	0.1246	FCC	1.8	+2
Pd	0.1376	FCC	2.2	+2
Zn	0.1332	HCP	1.6	+2

Callister & Rethwisch 5e.

1. Δr – slightly favors Al 近
2. Electronegativity – favors Al 近
3. Crystal structure – tie 平手
4. Valences – higher valance more soluble so favors Al 高價數

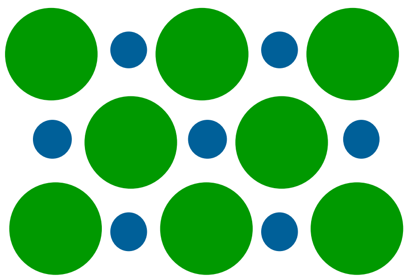
This suggests Al is more soluble in Zn.
This agrees with experimental observations.

5.4 Impurities in Solids

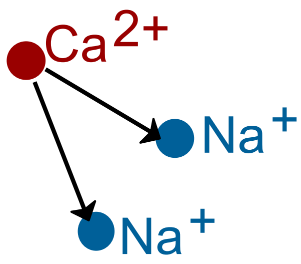
in Ceramics

- **Electroneutrality** (charge balance) must be maintained when impurities are present
- Ex: NaCl Na^+ Cl^-

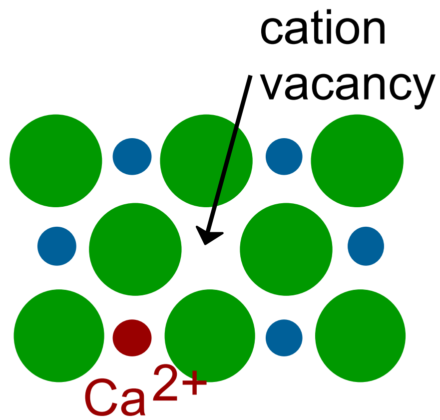
- Substitutional cation impurity



without impurity

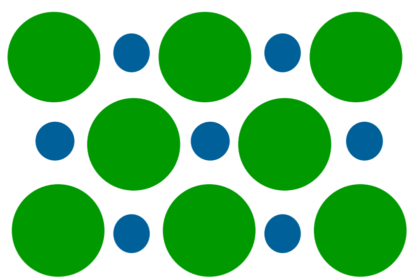


Ca^{2+} impurity

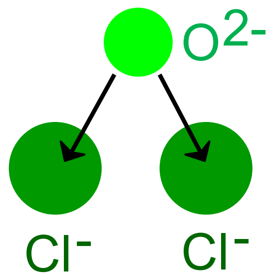


with impurity

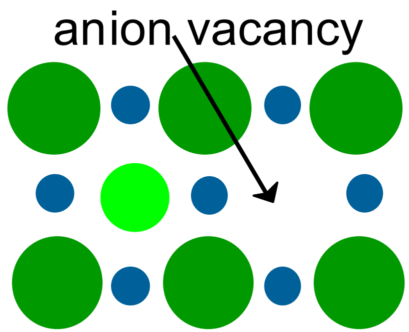
- Substitutional anion impurity



without impurity



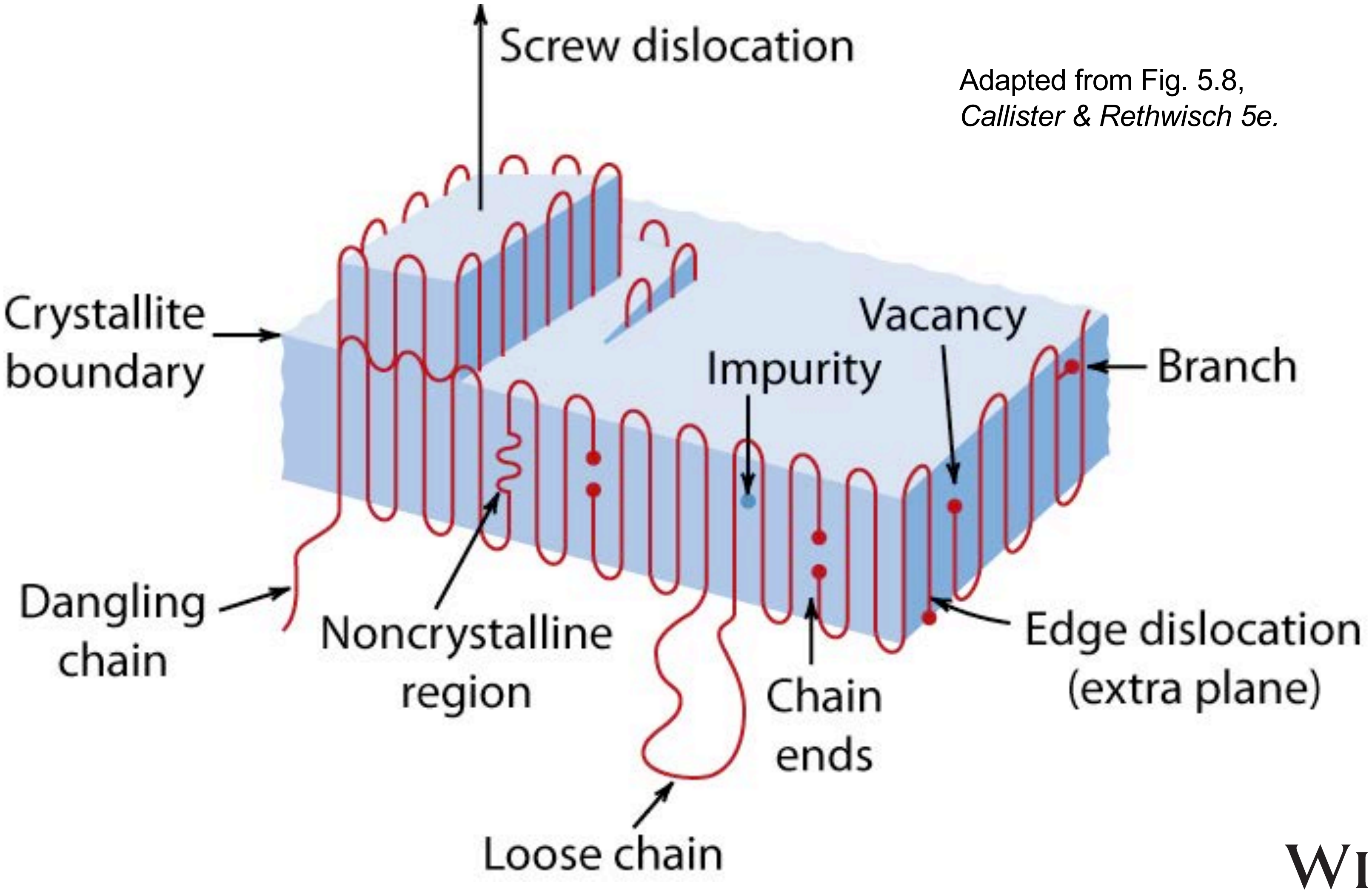
O^{2-} impurity



with impurity

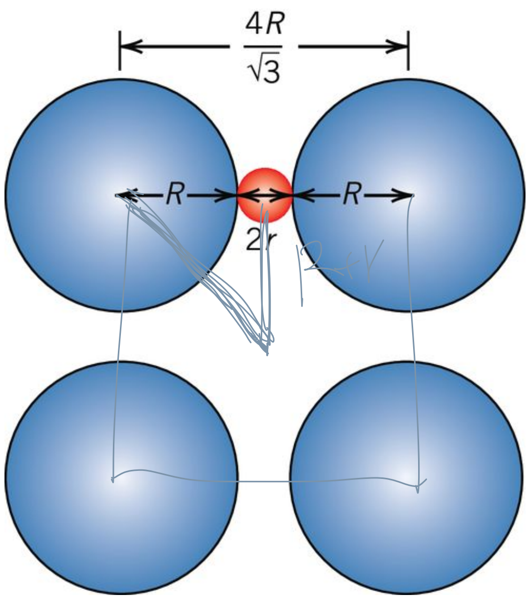
Point Defects in **Polymers**

- Defects due in part to ① **chain packing errors** and **impurities** such as ② chain ends and ③ side chains.



Adapted from Fig. 5.8, *Callister & Rethwisch 5e.*

Computation of radius of BBC interstitial site



Unit cell edge length $\quad a = \frac{4R}{\sqrt{3}}$ $\quad$ Eq 3.4

Unit cell edge length = $2R + 2r$

$$2R + 2r = \frac{4R}{\sqrt{3}}$$

$$2r = \frac{4R}{\sqrt{3}} - 2R = \left(\frac{2}{\sqrt{3}} - 1\right)(2R)$$

$\sqrt{(r+R)^2+R^2}$

$\frac{4R^2}{3} + \frac{1}{1}R^2 = \frac{7}{3}$

$r = 0.155R$

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Specification of Composition

The concentration of 1 in wt%, C_1

– **weight percent**

(wt%) C_1

$$C_1 = \frac{m_1}{m_1 + m_2} \times 100 \qquad (eq.\ 5.3)$$

m_1 = mass of component 1

Concentration of atom percent of element 1 in an alloy containing 1 and 2 atoms, C'_1

– **atom percent** C'_1

at%

$$C'_1 = \frac{n_{m1}}{n_{m1} + n_{m2}} \times 100 \qquad (eq.\ 5.5)$$

n_{m1} = number of moles of component 1

$$n_{m1} = \frac{m'_1}{A_1} \qquad (5.7)$$

m'_1 : mass (in grams)
A_1 :atomic weight,

EXAMPLE PROBLEME 5.5

Derive Eq. 5.9a

$$C_1' = \frac{C_1 A_2}{C_1 A_2 + C_2 A_1} \times 100 \qquad (5.9a)$$

推導C'$_1$

Total alloy mass (in grams)

$$M' = m'_1 + m'_2$$

$$n_{m1} = \frac{m'_1}{A_1} \qquad (5.7)$$

$$n = \frac{\text{質量}}{\text{重量}}$$

$$C_1' = \frac{n_{m1}}{n_{m1} + n_{m2}} \times 100 \qquad (eq.\ 5.5)$$

$$C'_1 = \frac{n_{m1}}{n_{m1} + n_{m2}} \text{ X } 100$$

$$= \frac{m'_1/A_1}{m'_1/A_1 + m'_2/A_2} \text{ X } 100$$

EXAMPLE PROBLEME 5.5

Derive Eq. 5.9a

$$C_1' = \frac{C_1 A_2}{C_1 A_2 + C_2 A_1} \times 100 \qquad (5.9a)$$

$$m'_1 = \frac{C_1 M'}{100}$$

$$C_1 = \frac{m'_1}{M'} \times 100$$

$m'_1 + m'_2$

$$C_1 = \frac{m_1'}{m_1' + m_2} \times 100$$

(eq. 5.3)

$$M' = m'_1 + m'_2$$

$$C'_1 = \frac{C_1 M'/100 A_1}{\dfrac{C_1 M'}{100 A_1} + \dfrac{C_2 M'}{100 A_2}} \times 100$$

$$C'_1 = \frac{C_1 A_2}{C_1 A_2 + C_2 A_1} \times 100$$

$$n_{m1} = \frac{m_1'}{A_1} \qquad (5.7)$$

m'_1 : mass (in grams)
A_1 :atomic weight,

Determine the composition, in atom %, of an alloy that consists of 97 wt.% aluminum and 3 wt.% copper

wt.%

$C_{Al}=97 \qquad C_{Cu}=3$

$$C'_{Al} = \frac{C_{Al}A_{Cu}}{C_{Al}A_{Cu} + C_{Cu}A_{Al}} \text{ X } 100$$

$$= \frac{(97)(63.55\text{ g/mol})}{(97)(63.55\text{ g/mol})+(3)(26.98\text{ g/mol})} \text{ x}100$$

$= 98.7$ at%

$$C'_{cu} = \frac{C_{Cu}A_{Al}}{C_{Cu}A_{Al} + C_{Al}A_{Cu}} \text{ X } 100$$

$$= \frac{(3)(26.98\text{ g/mol})}{(3)(26.98\text{ g/mol}) + (97)(63.55\text{ g/mol}} \text{ x}100$$

$= 1.30$ at%

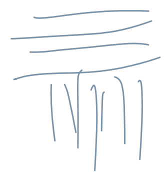
Miscellaneous imperfections

Linear Defects—Dislocations

Dislocations（差排）

- Are one-dimensional defects around which atoms are mis-aligned
  錯位

- Edge dislocation:（刀刃差排）
  - extra half-plane of atoms **inserted** in a crystal structure
  - **b** perpendicular (⊥) to dislocation line



- Screw dislocation（螺旋差排）
  - spiral planar ramp resulting from **shear deformation**
  - **b** parallel (||) to dislocation line

Burger’s vector, **b**: measure of lattice distortion
格子彎曲

Linear Defects—Dislocations

Edge Dislocation

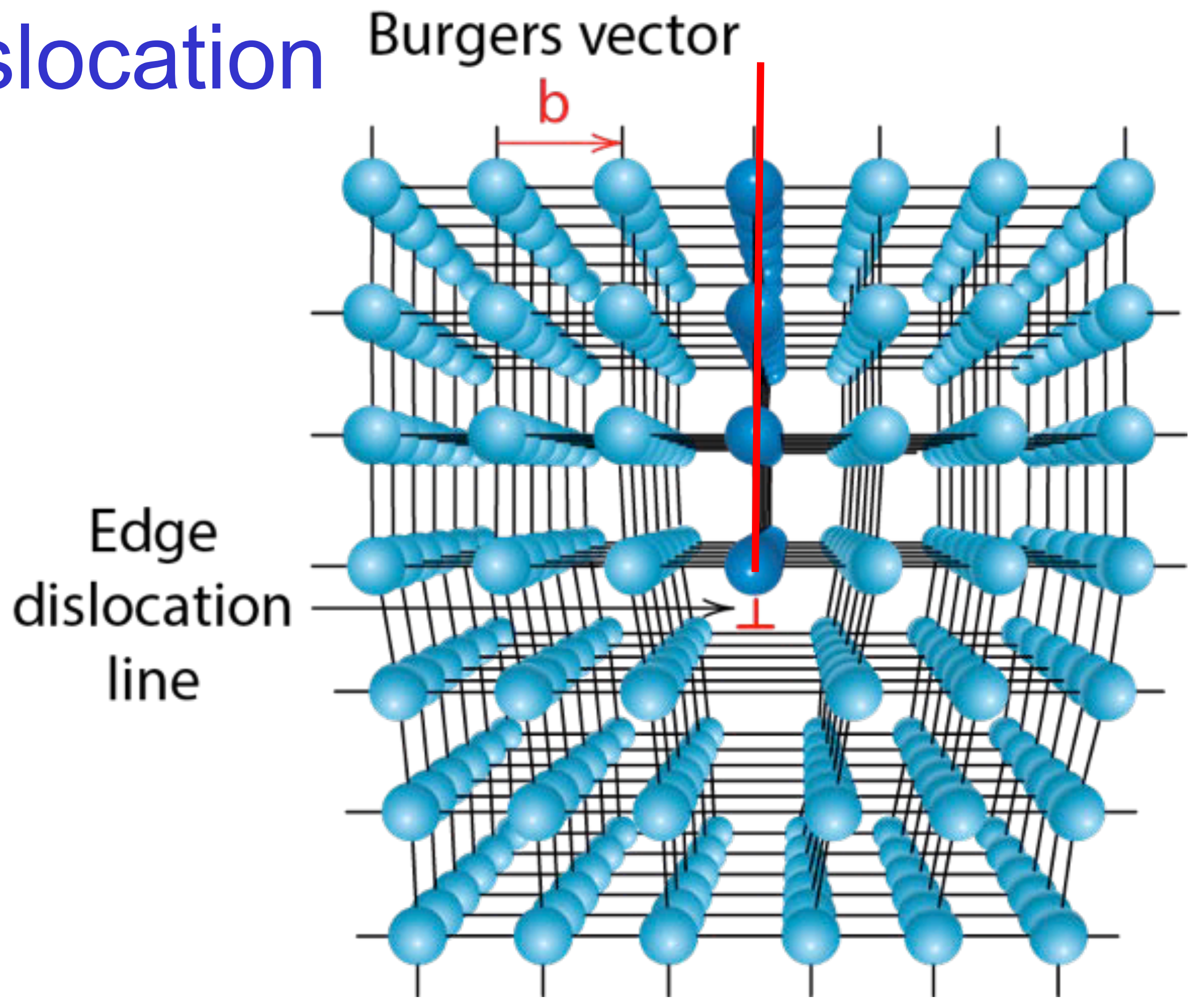


Fig. 5.9, *Callister & Rethwisch 5e.*

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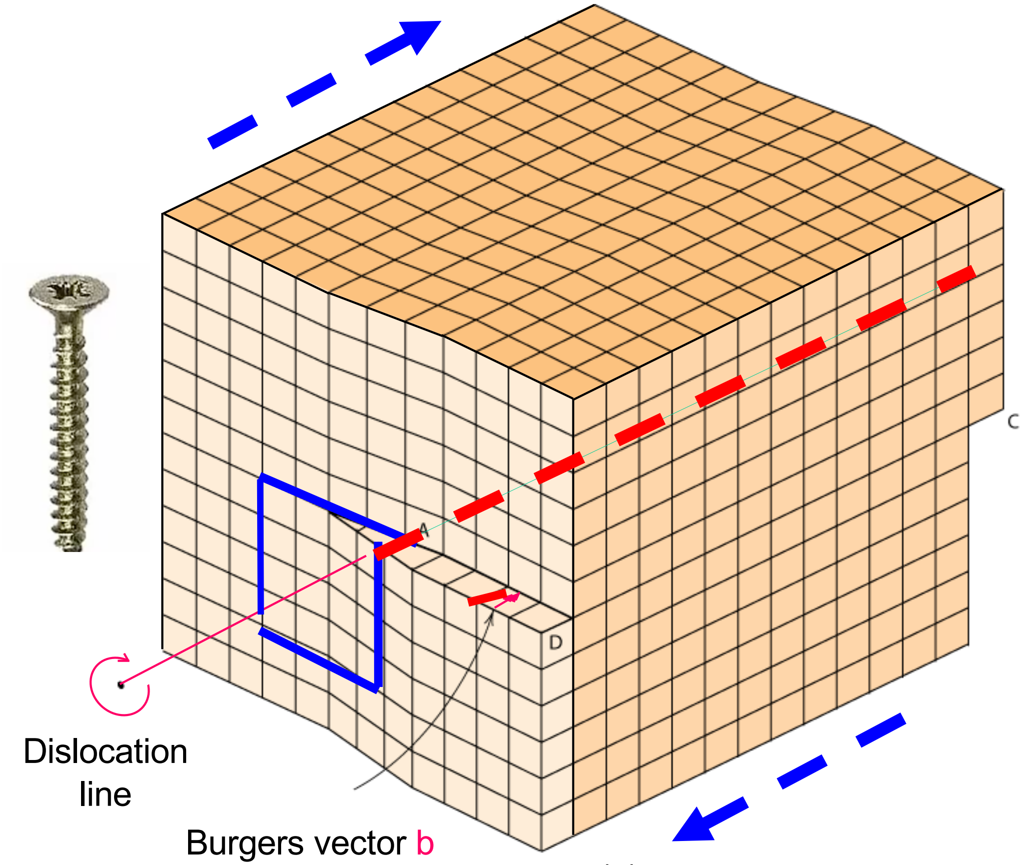
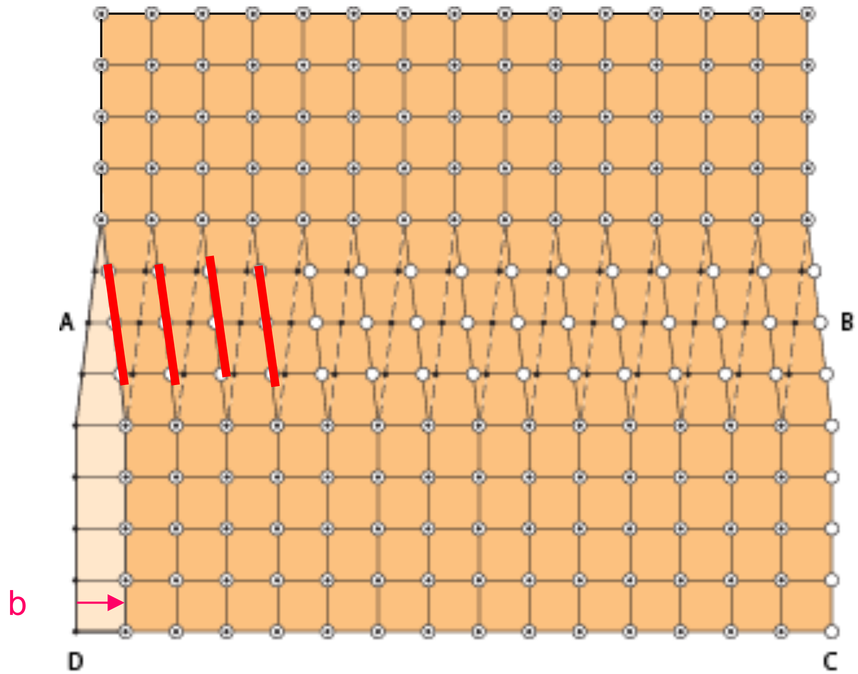
Screw Dislocation

(a) Schematic of screw dislocation in a crystal

(b) Top view of screw dislocation in (a)



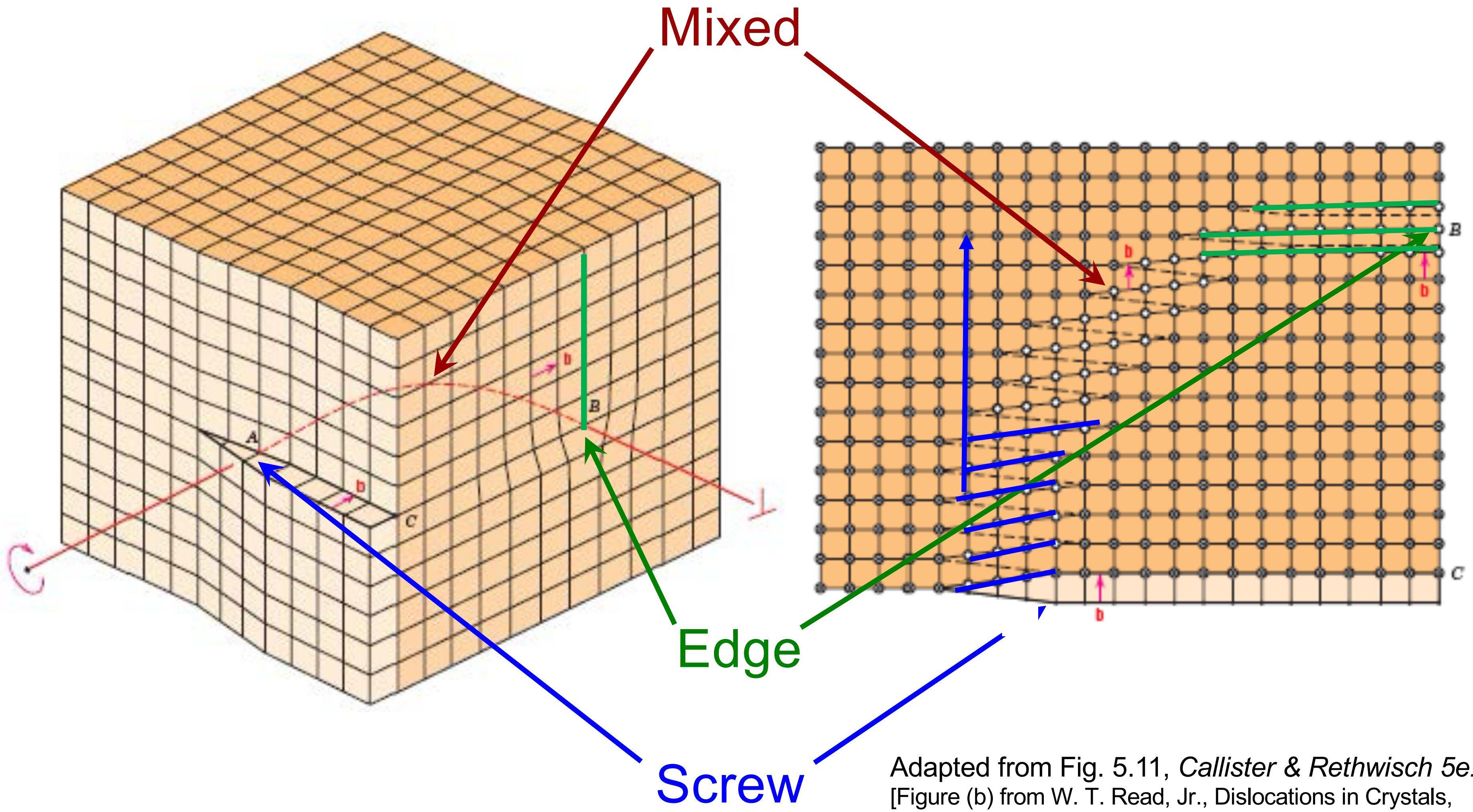
(a)



(b)

Adapted from Fig. 5.10, *Callister & Rethwisch 5e.*
[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. 5.11, *Callister & Rethwisch 5e.*
[Figure (b) from W. T. Read, Jr., Dislocations in Crystals, McGraw-Hill Book Company, New York, NY, 1953.]

Observation of Dislocations

Dislocations appear as dark lines
in this electron micrograph

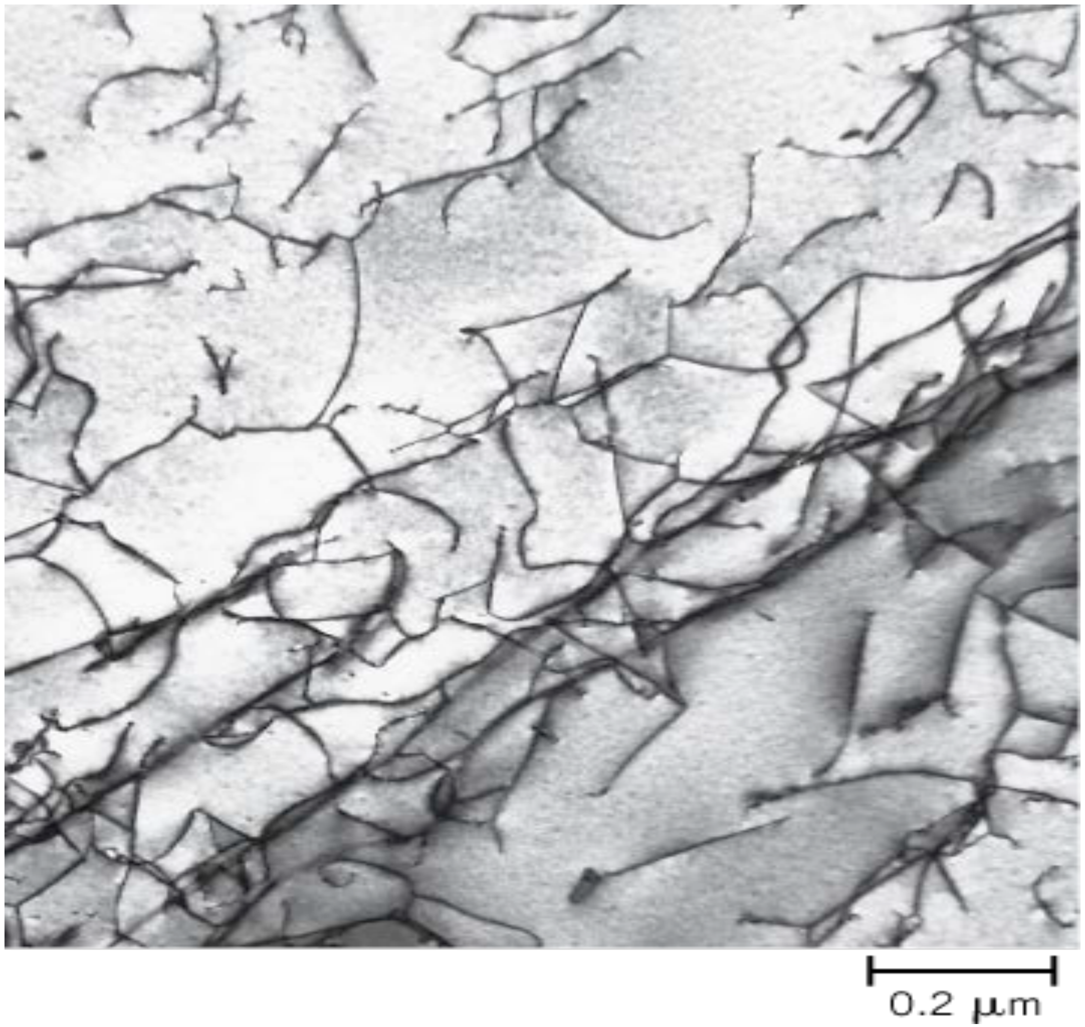


Fig. 5.12, *Callister & Rethwisch 5e.*
(Courtesy of M. R. Plichta, Michigan Technological University.)

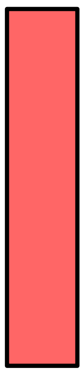
Linear Defects—Dislocations

Dislocations:

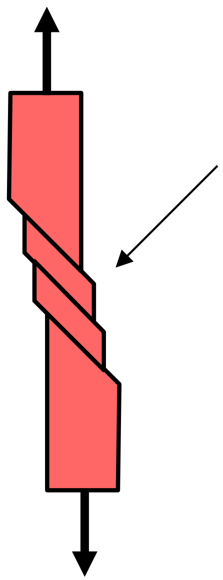
- move when **stresses** are applied,
- permanent (plastic) deformation results from dislocation motion.

Schematic of a single crystal metal

- **unstressed**
(un-deformed)



- **after tensile elongation**
(after plastic deformation)



Steps correspond to plastic deformation:

each step is produced by dislocations that have moved to the crystal surface.

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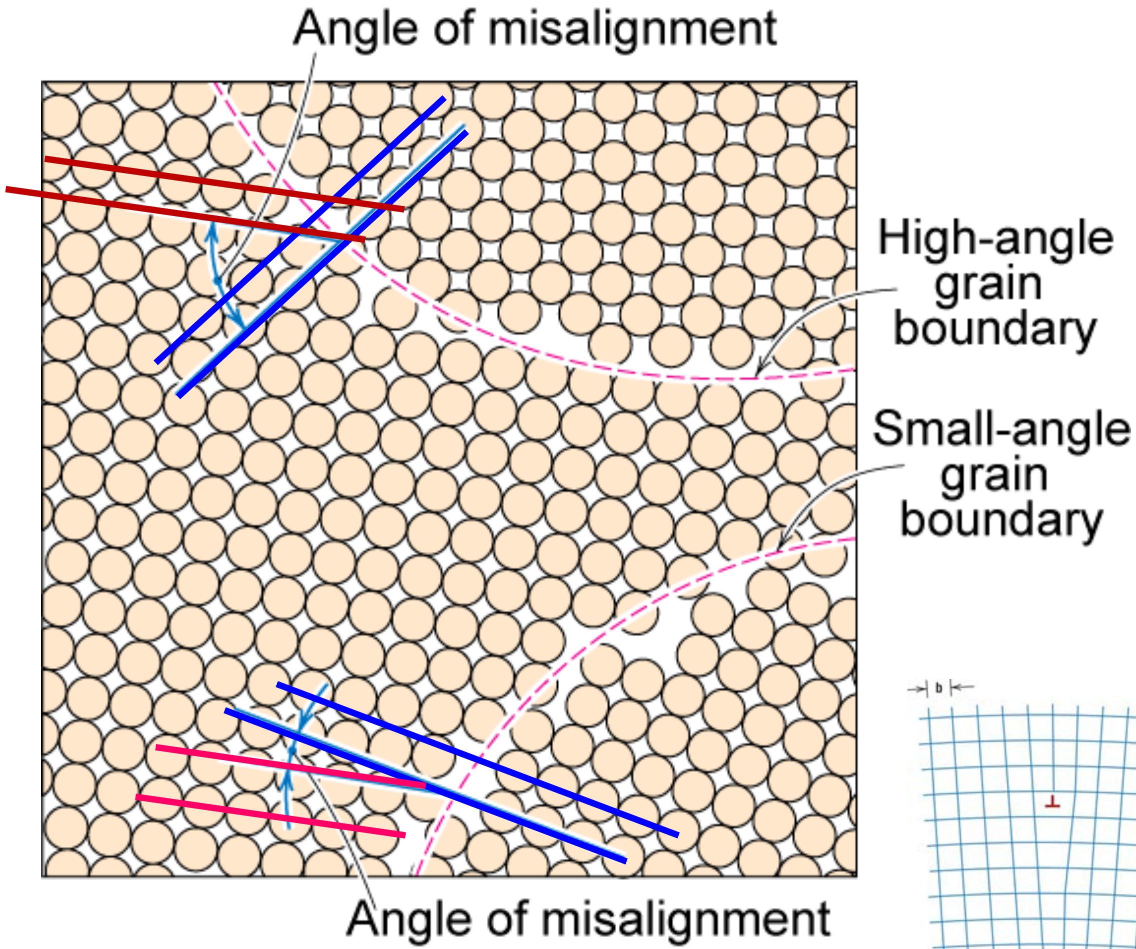
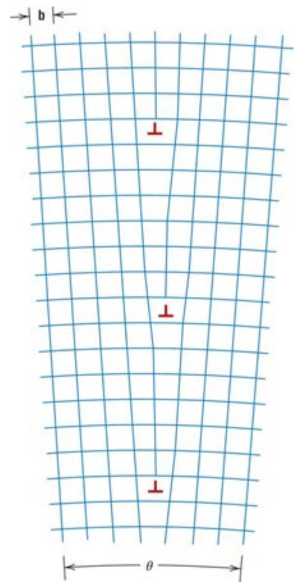
Grains and Grain Boundaries

Grain Boundaries

- Regions between grains (crystals)
- Crystallographic misalignment across a grain boundary
- Slight atomic disorder
  - high atomic mobility
  - high chemical reactivity



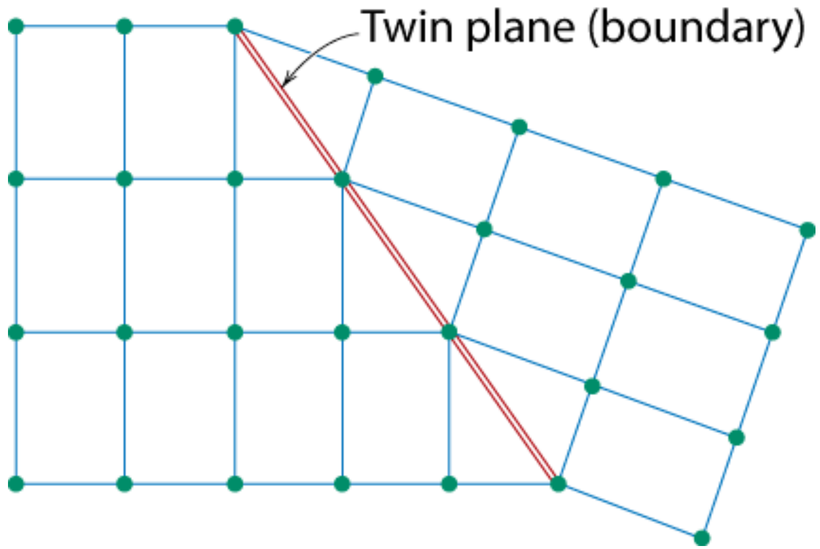
Adapted from Fig. 5.13, *Callister & Rethwisch 5e.*



Interfacial (Planar) Defects

- **Twin boundaries (or planes)** 孿晶界
  - Mirror reflections of atom positions of one side of twin plane to the other side.

Fig. 5.15, *Callister & Rethwisch 5e.*



(c)
Photomicrograph courtesy of J. E. Burke, General Electric Co.

- **Stacking faults** 疊差
  - Occur when there is an error in the planar stacking sequence
  - Ex: for FCC metals
    - normal sequence is ABCABC
    - becomes ABCABABC when there is a packing fault

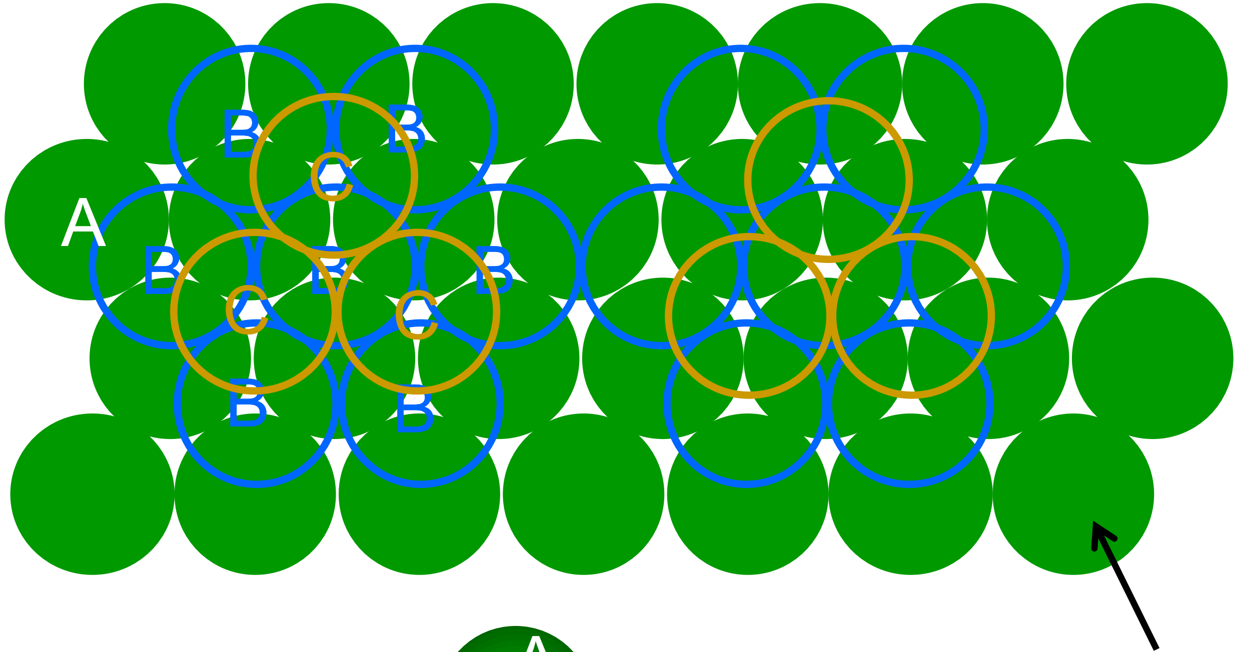
FCC Plane Stacking Sequence

- ABCABC... Stacking Sequence–Close-Packed Planes of Atoms
- 2D Projection

A sites

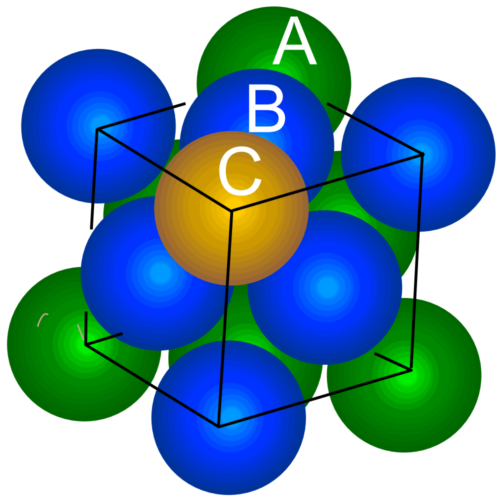
B sites

C sites



Close-Packed
Plane

- Stacking Sequence Referenced to an FCC Unit Cell.



WILEY

Catalysts and Surface Defects

催化劑

- A catalyst increases the rate of a chemical reaction without being consumed
- Catalytic reactions normally occur at surface defect sites

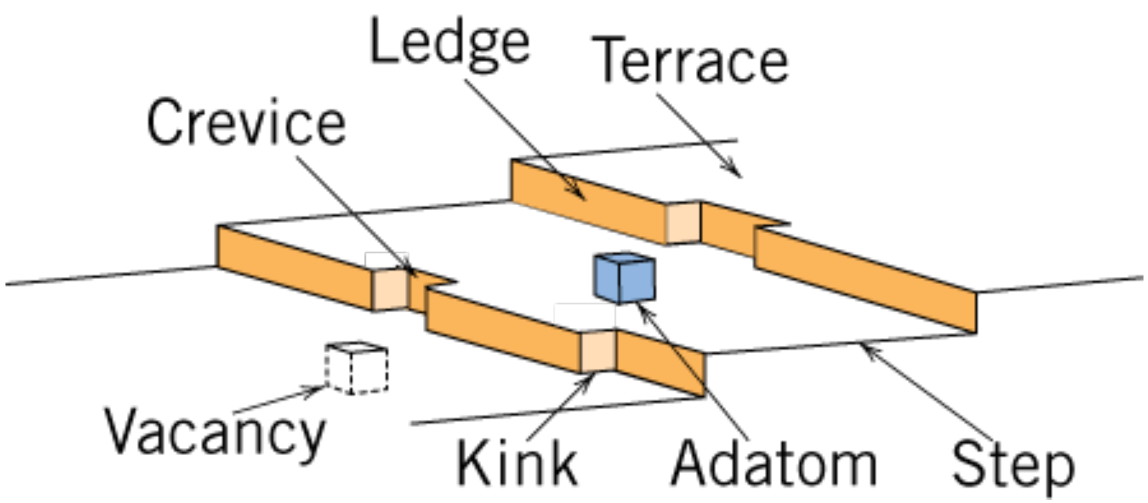


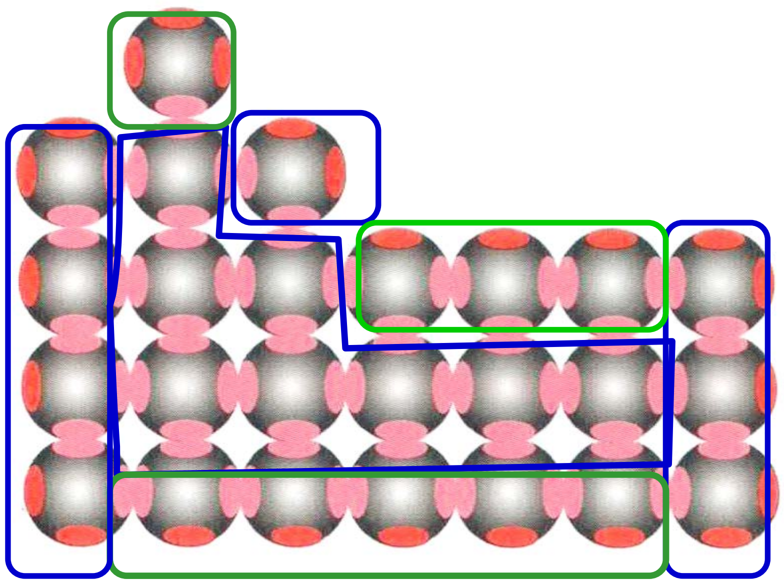
Fig. 5.16, *Callister & Rethwisch 5e.*

Surface Defects

The surface is the zone where the structure and composition, influenced by the interface, differs from the average (bulk) composition and structure.

體積

- The surface property is directly related to the bulk property since the surface is the discontinuous boundary between different phases.
- The surface of a material can be considered a type of planar defect.
- **Atoms at the surface are not bonded on all sides** to other atoms, there is extra energy (surface tension, g) associated with this region due to unfilled valence shells. (high reactivity)



Catalysts and Surface Defects

Single crystals of

$(Ce_{0.5}Zr_{0.5})O_2$

used in an automotive

catalytic converter

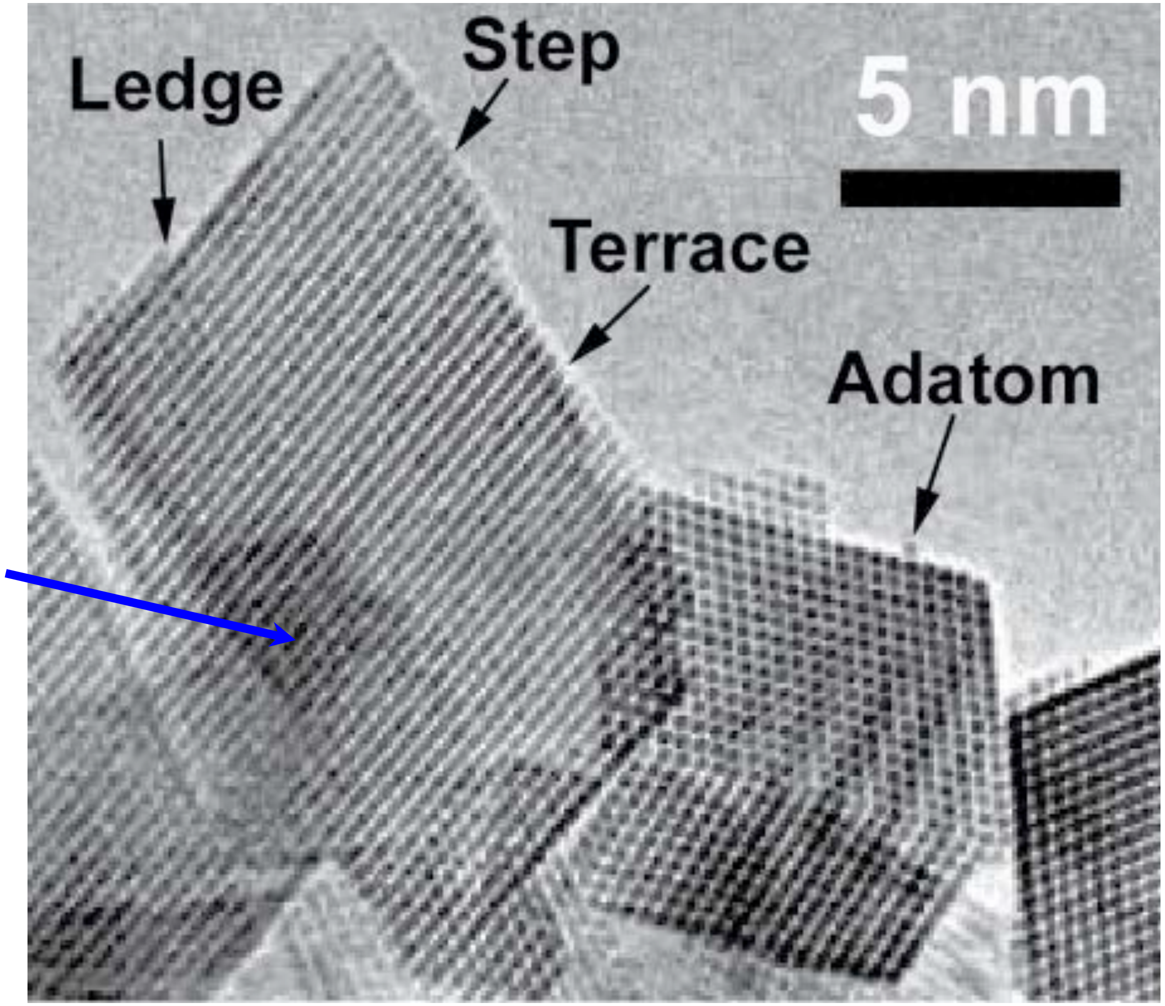


Fig. 5.17, *Callister & Rethwisch 5e.*
[From W. J. Stark, L. Mädler, M. Maciejewski, S. E. Pratsinis, and A. Baiker, "Flame Synthesis of Nanocrystalline Ceria/Zirconia: Effect of Carrier Liquid," Chem. Comm., 588–589 (2003). Reproduced by permission of The Royal Society of Chemistry.]

Microscopic Examination

Microscopy 顯微鏡學

microstructure

Microscopic Examination

調查

- Grain size is an important microscopic characteristic.
- Grain size can vary from one material to another.
  - Grain sizes can be quite large

    石英

    Ex: large single crystal of quartz or diamond or Si; individual grains visible in aluminum light posts and garbage cans

  - Grain sizes can be quite small (< μm);

    necessary to observe with a microscope.

Optical Microscopy 光學顯微鏡

- Uses light – useful up to 2000X magnification.
- Polishing removes surface features (e.g., scratches)
- Etching changes reflectance, depending on grain orientation.

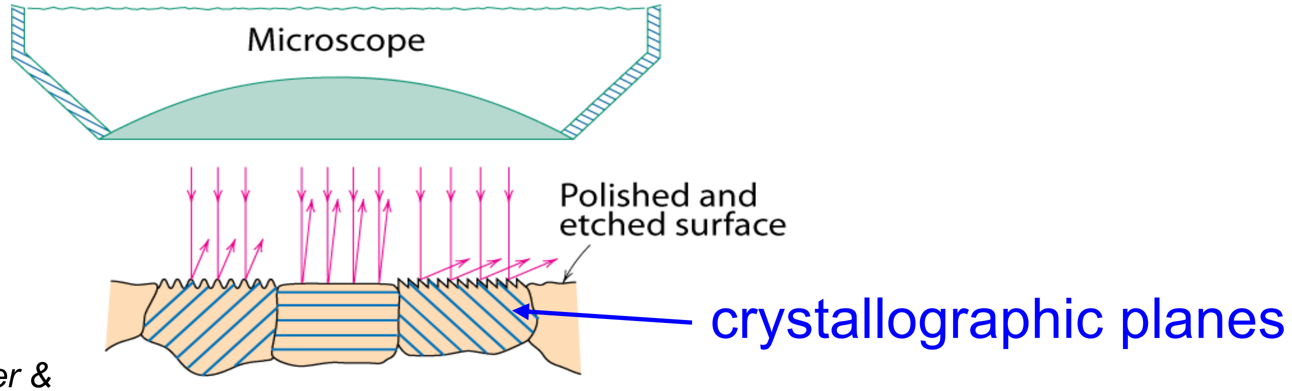
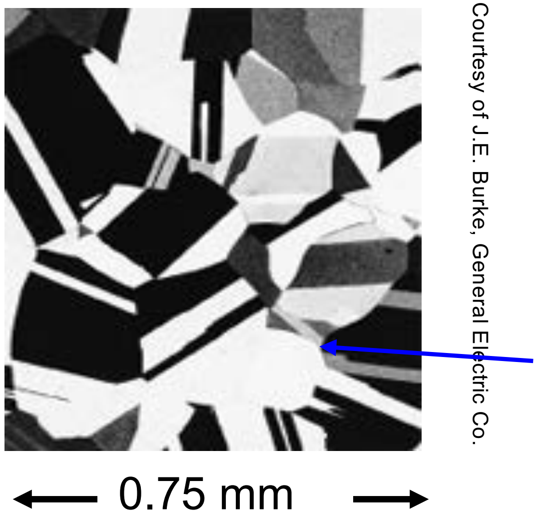


Fig. 5.19(b) & (c), *Callister & Rethwisch 5e.*

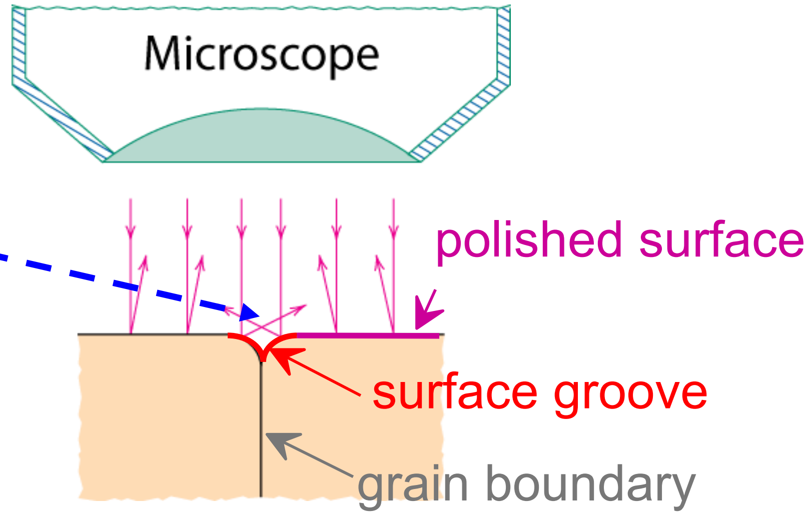


Microstructure of a brass alloy (a Cu-Zn alloy)

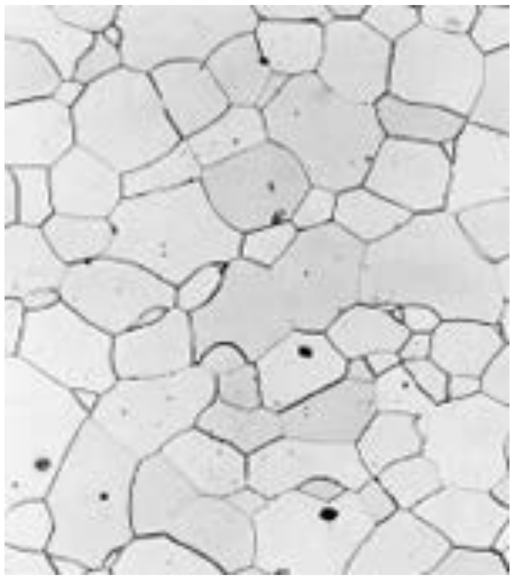
Optical Microscopy (cont.)

Grain boundaries...

- are more susceptible (影響) to etching 蝕刻
- after etching, grain boundaries appear as dark lines



(a)



(b)

Fe-Cr alloy

ASTM grain size number

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

number of grains/in^2 at 100x magnification

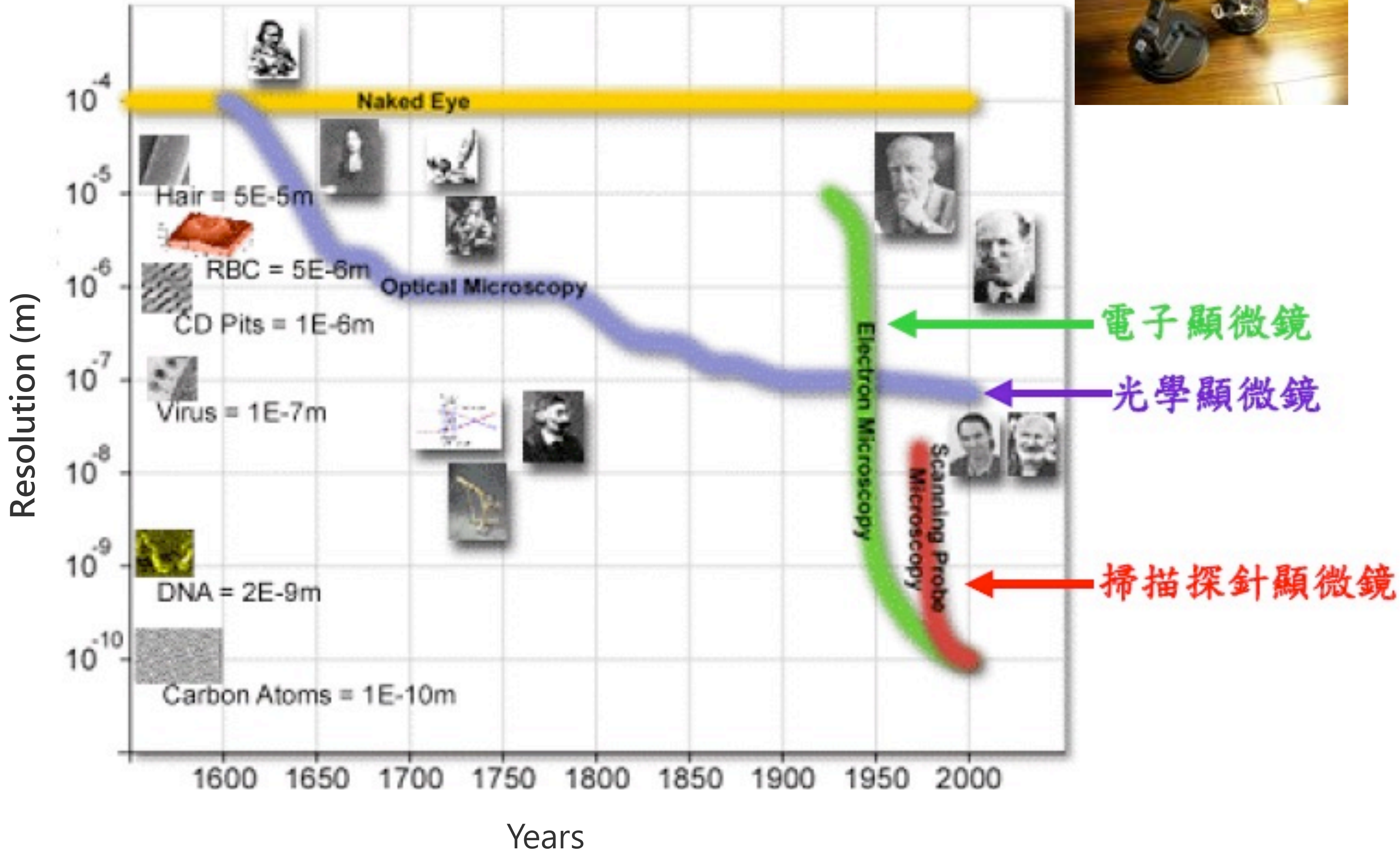
Fig. 5.20(a) & (b), *Callister & Rethwisch 5e.*
[Fig. 4.15(b) is courtesy of L.C. Smith and C. Brady, the National Bureau of Standards, Washington, DC (now the National Institute of Standards and Technology, Gaithersburg, MD).]

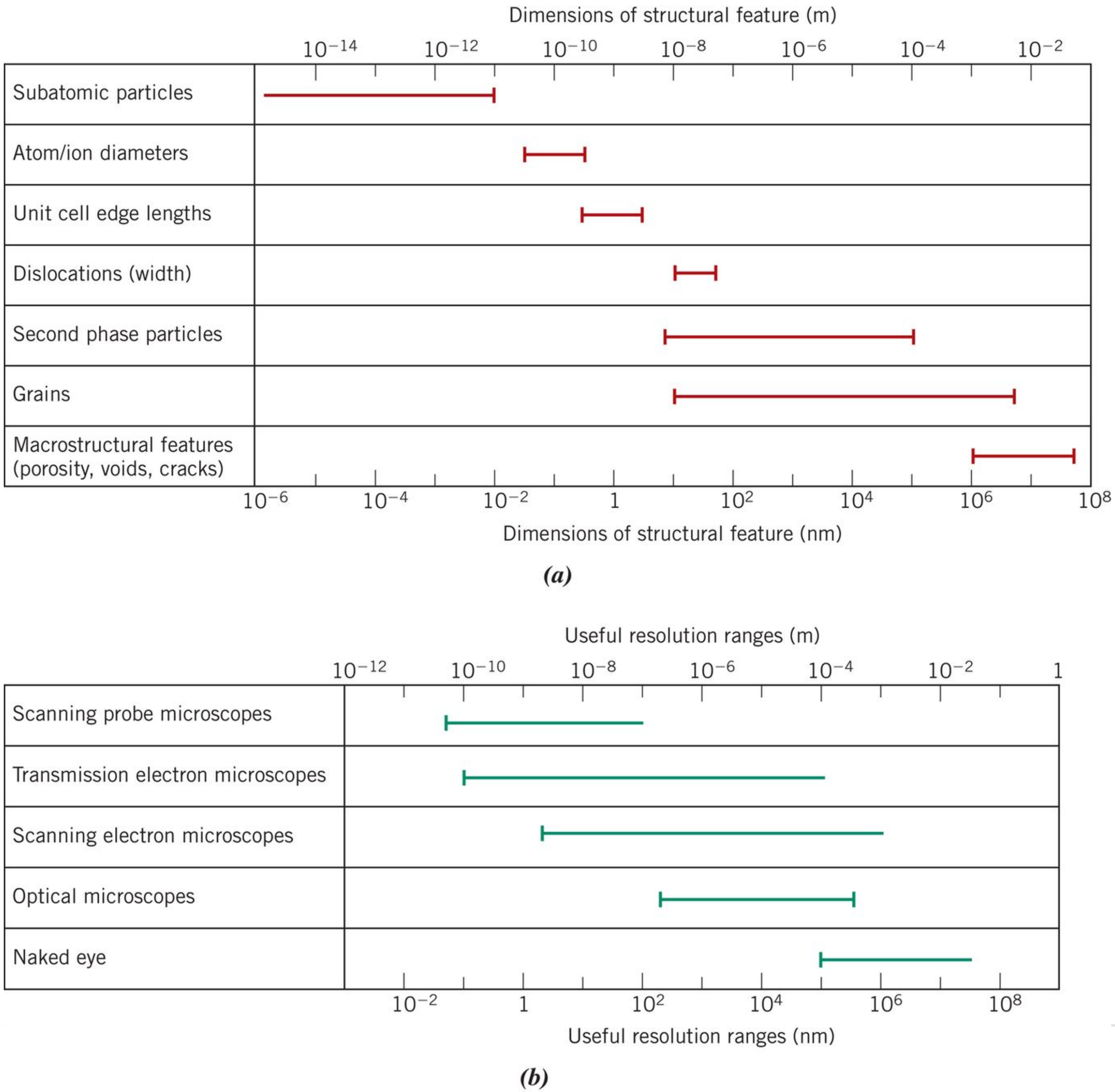
Optical Microscopy

- Polarized light
  - metallographic scopes often use polarized light to increase contrast
  - Also used for transparent sample polymers

顯微鏡的發展

1590年發明世上最早的顯微鏡





(Courtesy of Prof. Sidnei Paciornik, DCMM PUC-Rio, Rio de Janeiro, Brazil, and Prof. Carlos Pérez Bergmann, Federal University of Rio Grande do Sul, Porto Alegre, Brazil.)

Fig_5-21

Types of Microscope (顯微鏡的種類)

- Optical Microscope (OM) 光學顯微鏡
- Scanning Electron Microscope (SEM) 掃描式電子顯微鏡
- Transmission Electron Microscope (TEM) 穿透式電子顯微鏡
- Scanning Transmission Electron Microscope (STEM) 掃描穿透式電子顯微鏡
- Scanning Probe Microscope (SPM,) 掃描探針顯微鏡

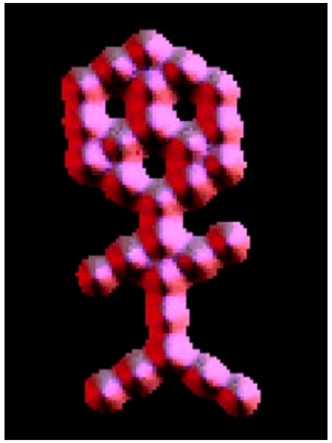
Electron Microscopy

- Best resolution for optical microscopes is
  ≈ 0.1 µm   (100 nm)

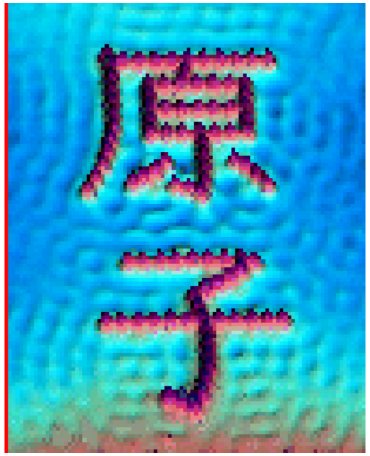
- For higher resolution need to use shorter wavelength radiation
  - X-Rays? Difficult to focus.
  - Electron beams
    - Wavelengths as short as 3 pm (0.003 nm) possible
      - (Magnification as high as 1,000,000X are achievable)
    - Atomic resolution possible
    - Electron beams focused by magnetic lenses.

Scanning Tunneling Microscopy(STM)

- Surface atoms imaged using a microprobe that tapers to a single atom at its tip.
- Surface atoms can be rearranged by pushing them into the desired position using the probe tip.



Carbon monoxide molecules arranged on a platinum surface in the form of a human.



Iron atoms arranged on a copper surface to form the Japanese Kanji characters that represent the word “atom”.

Photos produced from the work of C.P. Lutz, Zeppenfeld, and D.M. Eigler. Reprinted with permission from International Business Machines Corporation, copyright 1995.

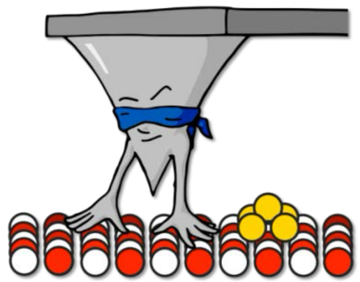
Scanning Probe Microscopy (SPM)

Advantage

- Probe scanning
- Non-vacuum environment
- 3 D
- Liquid condition
- Biological interaction

Disadvantage

- Topography observation, couldn't analyze internal compartment.
- Anti-vibration



Summary

- **Point**, **Linear**, **and Interfacial defects exist in solids.**

- Point defects
  - Vacancies
  - Interstitial atoms
  - Substitutional impurity atoms

- Linear defects
  - Dislocations
- Interfacial defects
  - Grain boundaries
  - Twin boundaries
  - Stacking Faults

- The equilibrium number vacancy defects depends on temperature

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

- Dislocation types include edge, screw, and mixed