Imperfections in Solids

Dr. Arindam Ghosal

Imperfections in Solids

- The properties of some materials are profoundly influenced by the presence of imperfections.
- It is important to have knowledge about the types of imperfections that exist and the roles they play in affecting the behavior of materials.

Atom Purity and Crystal Perfection

- If we assume a perfect crystal structure containing pure elements, then anything that deviated from this concept or intruded in this uniform homogeneity would be an imperfection.
  1. There are no perfect crystals.
  2. Many material properties are improved by the presence of imperfections and deliberately modified (alloying and doping).

Types of Imperfections

- Vacancy atoms
- Interstitial atoms
- Substitutional atoms

Point defects
1-2 atoms

- Dislocations

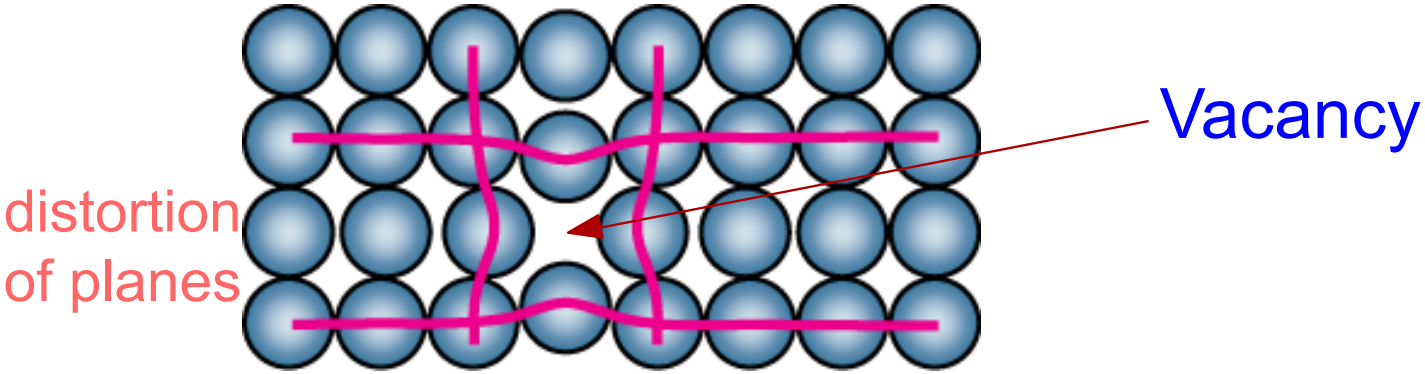
Line defects
1-dimensional

- Grain Boundaries

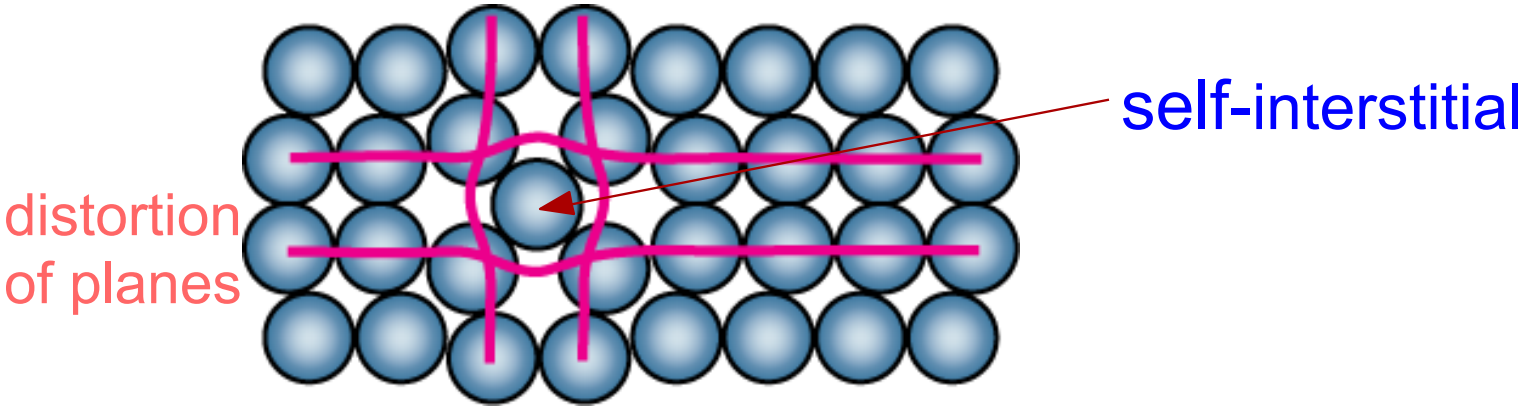
Area defects
2-dimensional

Point Defects in Metals

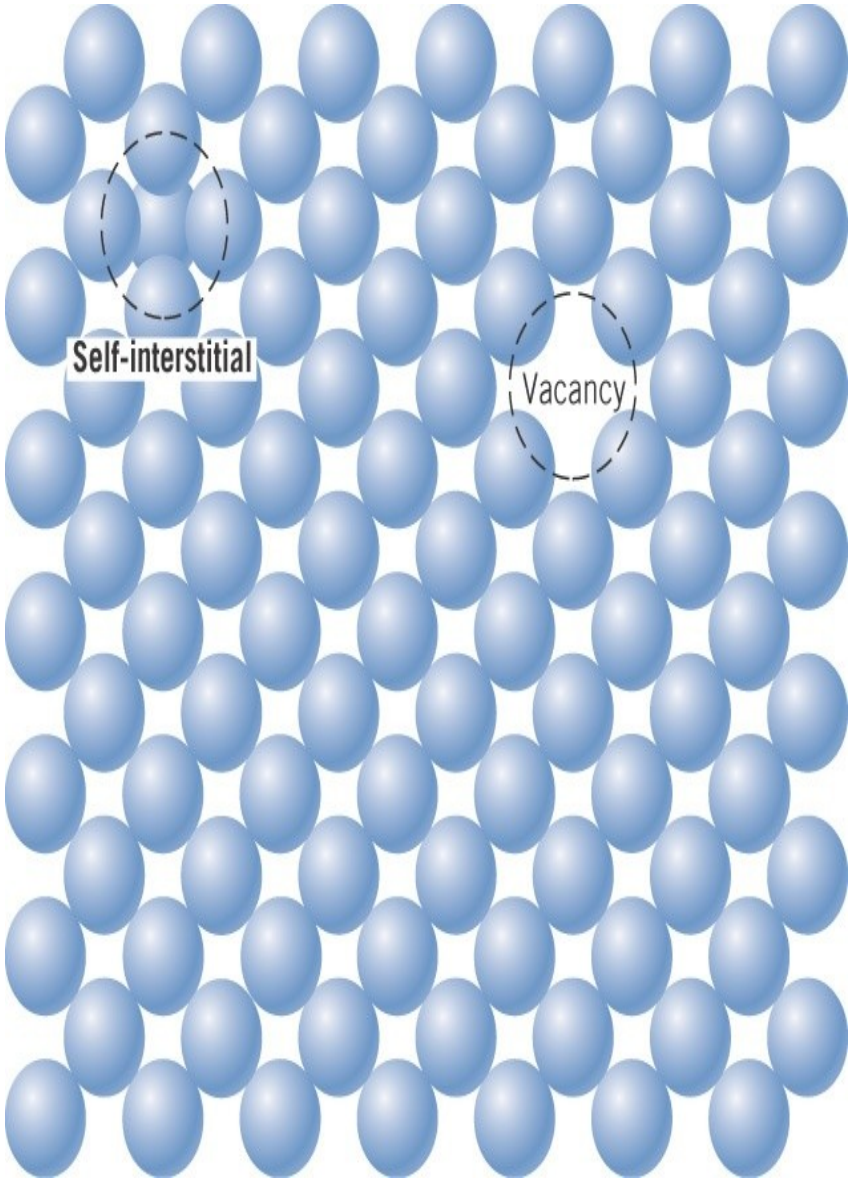
- Vacancies:
  -vacant atomic sites in a structure.



- Self-Interstitials:
  -"extra" atoms positioned between atomic sites.



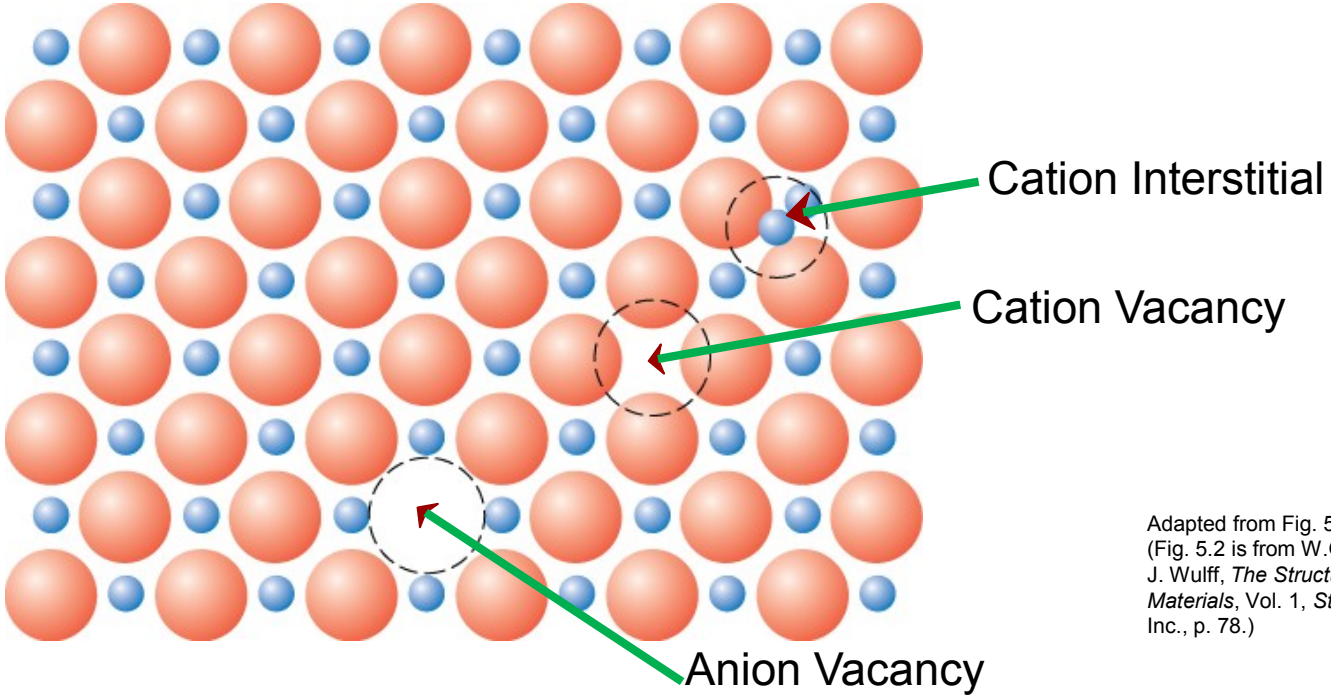
Self Interstitials



- In metals, a self interstitial introduces relatively large distortions (strain) in the surrounding lattice since the atom is substantially larger than the interstitial site.

Point Defects in Ceramics

- Vacancies
  -- vacancies exist in ceramics for both cations and anions
- Interstitials
  -- interstitials exist for cations
  -- interstitials are not normally observed for anions because anions are large relative to the interstitial sites



Adapted from Fig. 5.2, *Callister & Rethwisch 3e.* (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.)

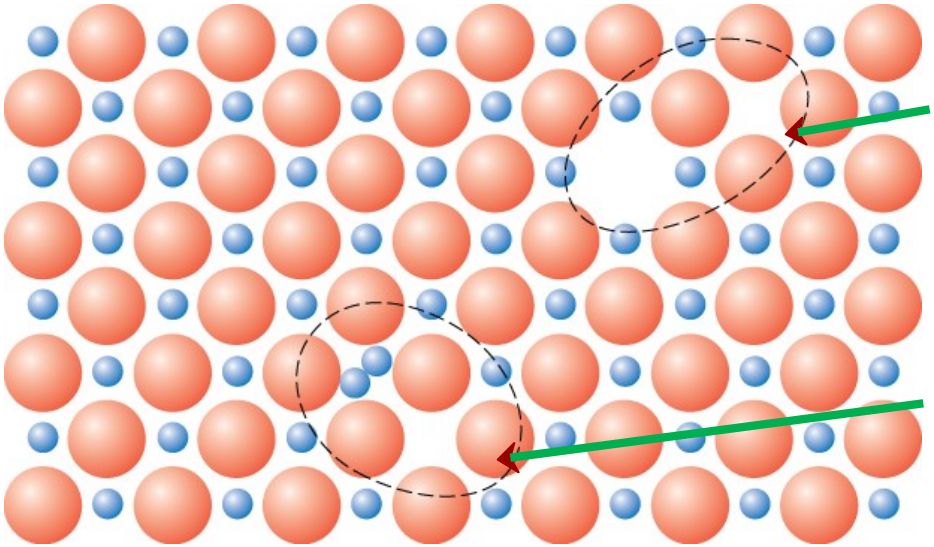
Point Defects: Frenkel and Schottky

- **Frenkel Defect**

To maintain the charge neutrality, a cation vacancy-cation interstitial pair occur together. The cation leaves its normal position and moves to the interstitial site.

- **Schottky Defect**

To maintain the charge neutrality, remove 1 cation and 1 anion; this creates 2 vacancies.



Adapted from Fig. 5.3, *Callister & Rethwisch 3e.* (Fig. 5.3 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.)

Equilibrium Concentration: Point Defects

- Equilibrium concentration varies with temperature.

Activation energy – energy required for formation of vacancy

No. of defects

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

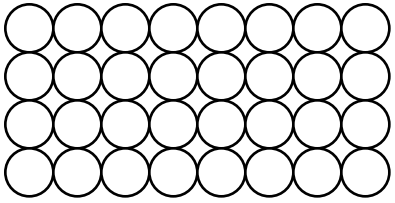
No. of potential defect sites

Temperature

Boltzmann's constant

(1.38 x 10^{-23} J/atom-K)

(8.62 x 10^{-5} eV/atom-K)



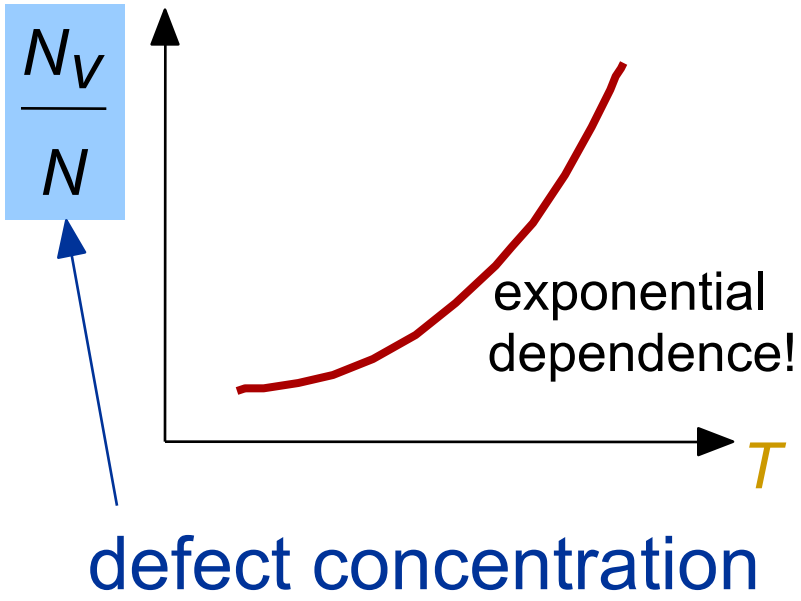
Each lattice site is a potential vacancy site

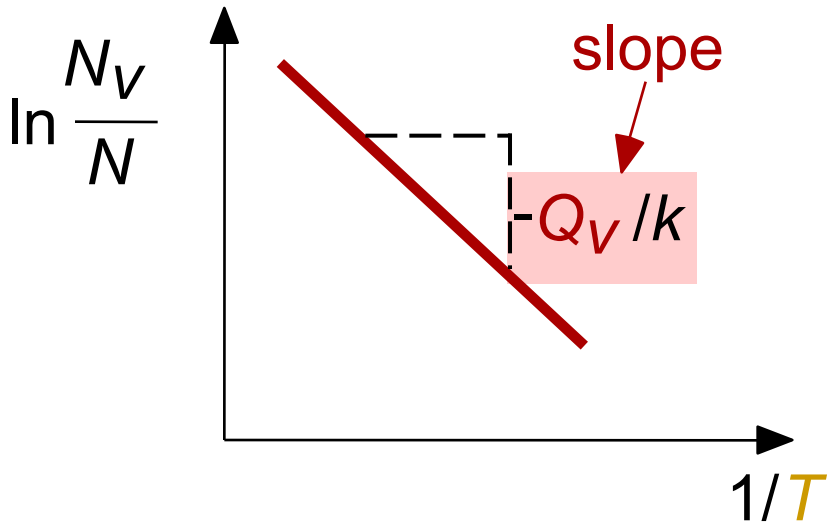
Measuring Activation Energy

- We can get Q_v from an experiment.
- Measure this...

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

- Replot it...





Estimating Vacancy Concentration

- Find the equil. # of vacancies in 1 m^3 of Cu at 1000°C.
- Ex 5.1 - Given:

$\rho = 8.4\ g/cm^3$ $\quad A_{Cu} = 63.5\ g/mol$

$Q_V = 0.9\ eV/atom$ $\quad N_A = 6.02 \times 10^{23}\ atoms/mol$

$$\frac{N_V}{N} = \exp\left(\frac{-Q_V}{kT}\right) = 2.7 \times 10^{-4}$$

0.9 eV/atom

1273 K

8.62×10^{-5} eV/atom-K

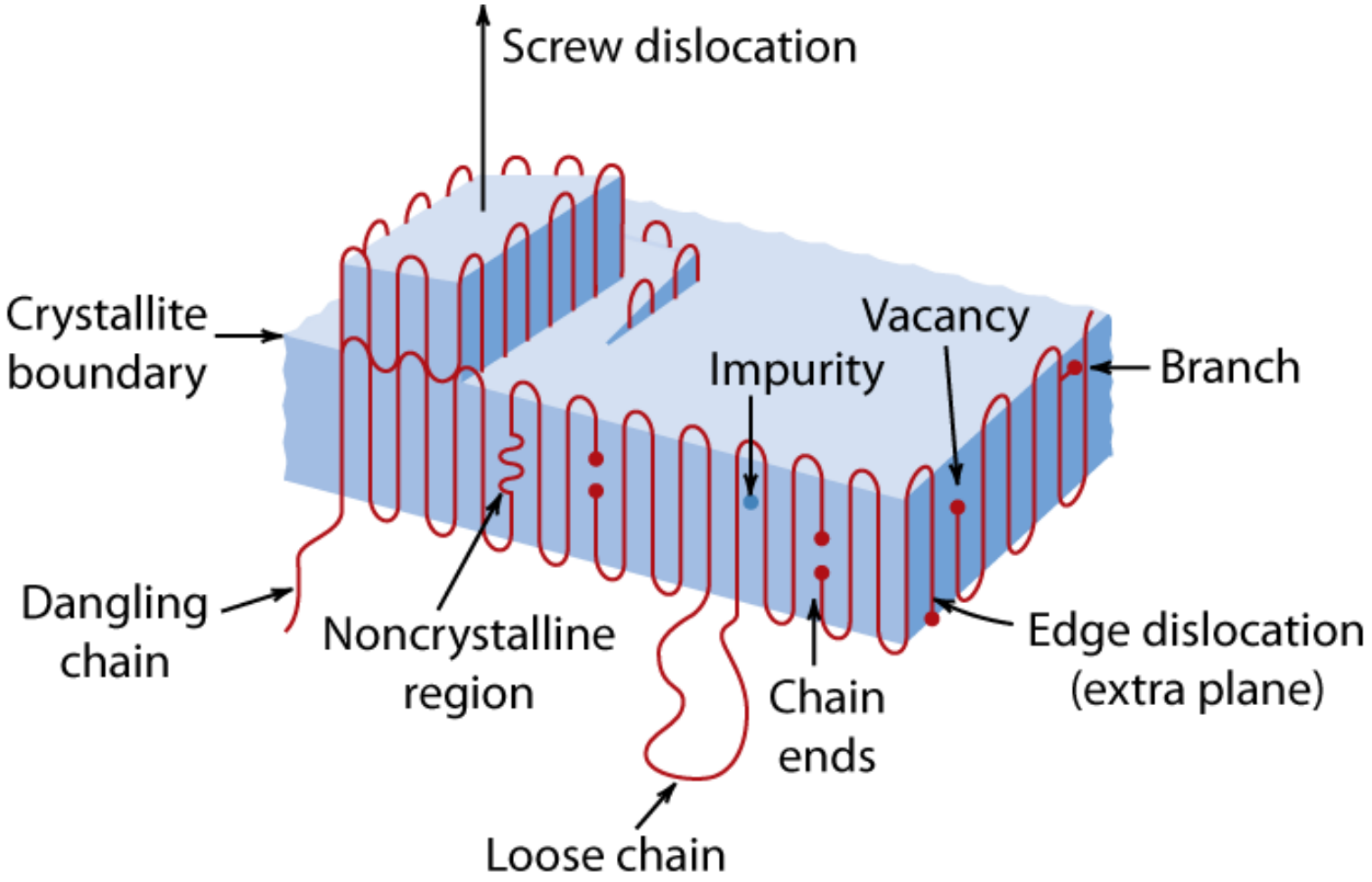
For 1 m^3, $N = \rho \times \frac{N_A}{A_{Cu}} \times 1\ m^3 = 8.0 \times 10^{28}$ sites

- Answer:

$N_V = (2.7 \times 10^{-4})(8.0 \times 10^{28})$ sites $= 2.2 \times 10^{25}$ vacancies

Point Defects in Polymers

- Defects due in part to chain packing errors and impurities such as chain ends and side chains



Alloying

- Given a metal (with only 1 type of atom) refined to 99.9999% purity, there would still exist 10^{22} to 10^{23} impurity atoms in 1 cubic meter of material.
- Most metals are alloys. Alloying is done to improve strength, corrosion resistance, ductility, lower melting T.
- For example, sterling silver is an alloy of 92.5% silver, 7.5% copper. At room temperature, “pure” silver is highly corrosion resistant, but also very soft. The addition of copper improves the strength and maintains good corrosion behavior.

Solid Solution

- The addition of impurity atoms to a metal results in the formation of a solid solution.
- The solvent represents the element that is present in the greatest amount (the host atoms). For example, in Lab 8 (MSE 227) Precipitation Hardening of Aluminum, aluminum is the solvent and copper is the solute (present in minor concentration).
- Solid solutions form when the solute atoms (Cu) are added to the solvent (Al), assuming the crystal structure is maintained and no new structures are formed.

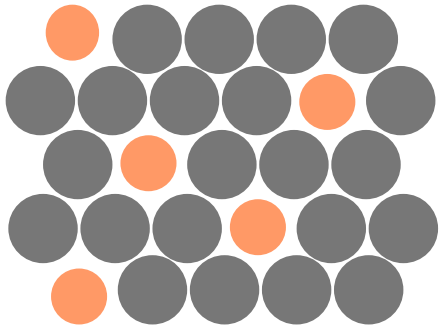
Solid Solution - continued

- A solid solution is a homogenous composition throughout.
- The impurity atoms (Cu) are randomly and uniformly dispersed within the solid.
- The impurity defects in the solid solution are either substitutional or interstitial.

Imperfections in Metals

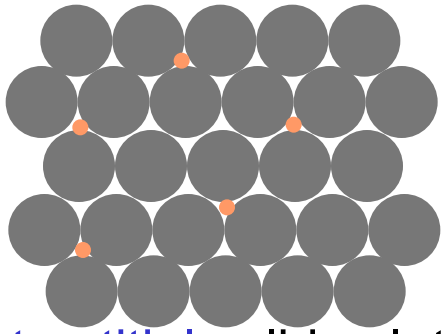
What are the outcomes if impurity (B) is added to host (A)?

- Solid solution of B in A (random distribution of point defects)



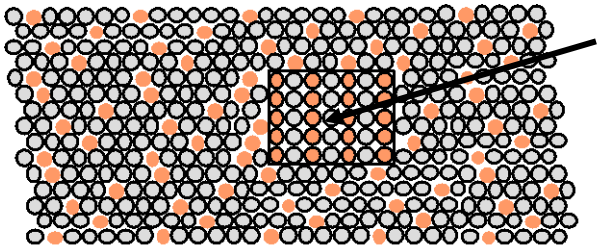
Substitutional solid solution.
(e.g., Cu in Ni)

OR



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

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



Second phase particle
-- different composition
-- often different structure.

Hume - Rothery Rules

The **Hume-Rothery rules** are basic conditions for an element to dissolve in a metal, forming a substitutional solid solution.

1. The atomic radius of the solute and solvent atoms must differ by no more than 15% ($\Delta r < 15\%$).
2. The solute and solvent should have similar electronegativities.
3. Same crystal structure for "pure" metals.
4. Maximum solubility occurs when the solvent and solute have the same valence. Metals with lower valence will tend to dissolve metals with higher valence.

Substitutional Solid Solution Example: Copper and Nickel

Element	*Atomic Radius (nm)*	*Crystal Structure*	*Electro-nega-tivity*	*Valence*
Cu	0.1278	FCC	1.9	+2
C	0.071		2.5	
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

Interstitial Solid Solution

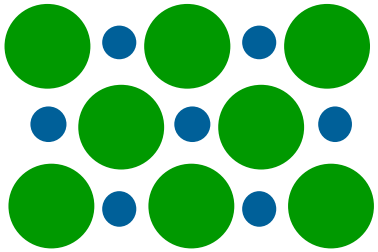
- Carbon forms an interstitial solid solution when added to iron; the maximum concentration of carbon that can be added is roughly 2%.
- The atomic radius of the carbon atom is much less than that of iron (0.071nm vs 0.124 nm).
- For interstitial solid solutions, the Hume-Rothery rules are:
  - 1. Solute atoms must be smaller than the pores in the solvent lattice.
  - 2. The solute and solvent should have similar electronegativity.

Imperfections in Ceramics

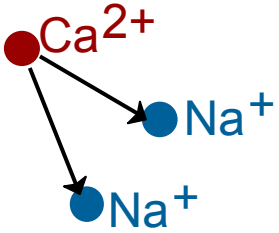
- Since there are both anions and cations in ceramics, a substitutional impurity will replace the host ion most similar in terms of charge.
- Charge balance must be maintained when impurities are present.

- Ex: NaCl

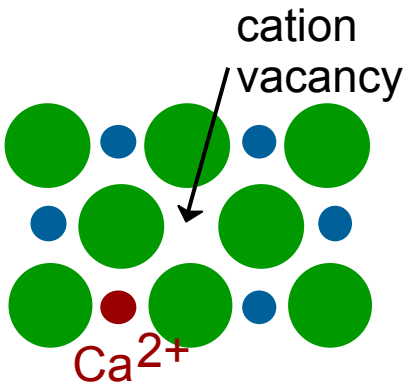
- Substitutional cation impurity



without impurity

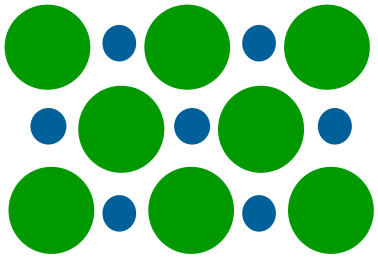


Ca^{2+} impurity

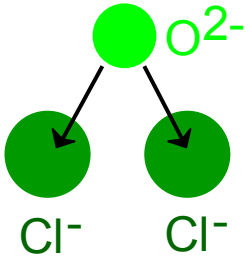


with impurity

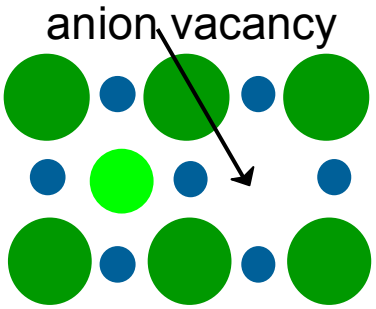
- Substitutional anion impurity



without impurity

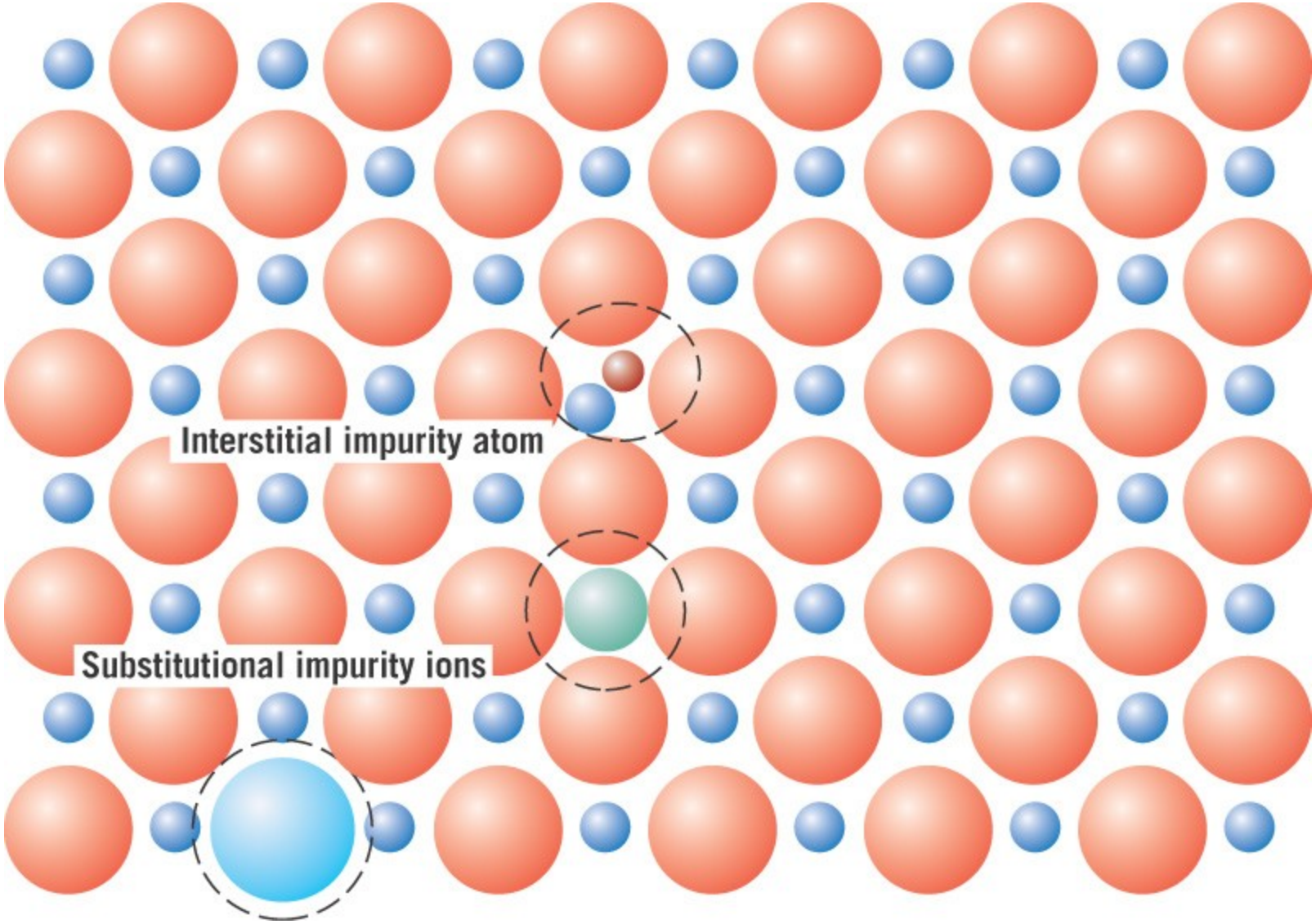


O^{2-} impurity



with impurity

Point Defects: Impurities



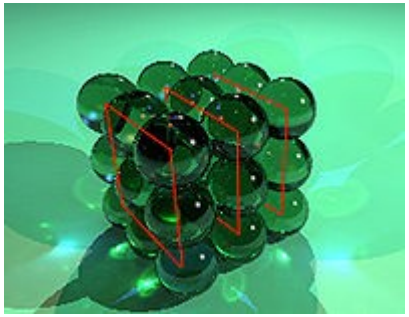
Types of Imperfections

- Vacancy atoms
- Interstitial atoms
- Substitutional atoms

Point defects
1-2 atoms

- Dislocations

Line defects
1-dimensional



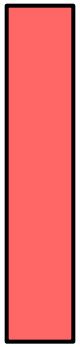
Line Defects

Dislocations:

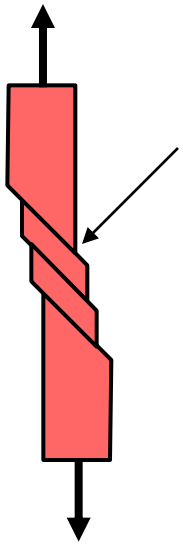
- are line defects,
- slip between crystal planes result when dislocations move,
- produce permanent (plastic) deformation.

Schematic of Zinc (HCP):

- before deformation



- after tensile elongation

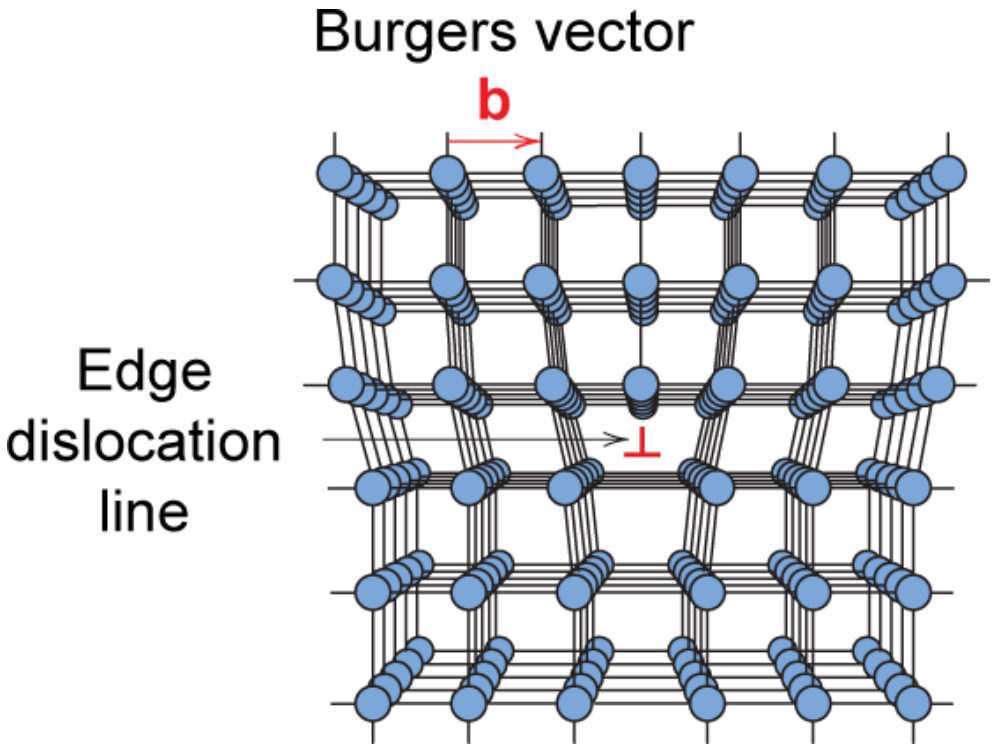


Imperfections in Solids

Linear defects (Dislocations) are one-dimensional defects that cause misalignment of nearby atoms.

Linear defects are associated primarily with **mechanical deformation.**

Types of dislocations: edge, screw, mixed.



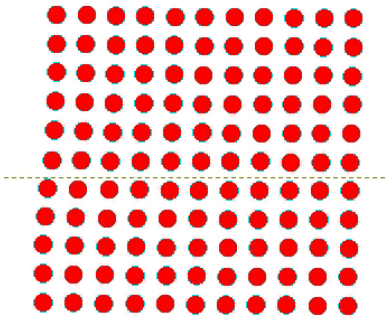
Edge dislocation:

- extra half-plane of atoms inserted in a crystal structure; the edge of the plane terminates within the crystal.
- Around the dislocation line there is some localized distortion.
- **b** perpendicular (⊥) to dislocation line

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

Motion of Edge Dislocation

- Dislocation motion requires the successive bumping of a half plane of atoms (from left to right).
- Bonds across the slipping planes are broken and remade in succession.
- The (plastic) permanent deformation of most crystalline materials is by dislocation movement.
- Most contain some dislocations that were introduced during solidification, plastic deformations, and rapid cooling (thermal stresses).
- To deform plastically means to slide atomic planes past each other.



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

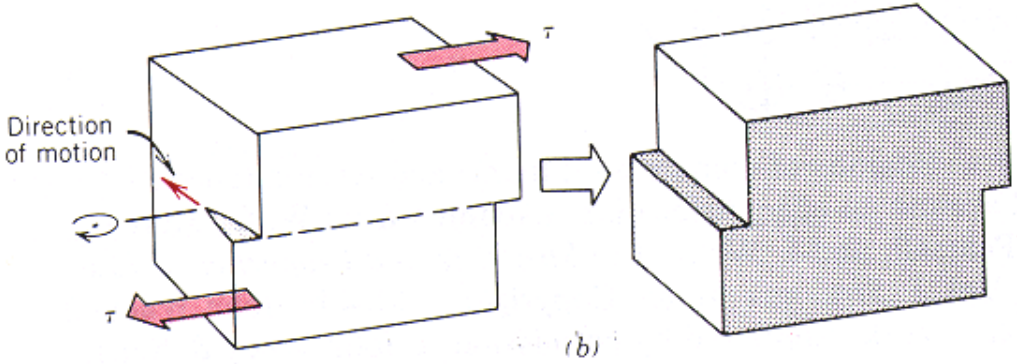
Dislocations

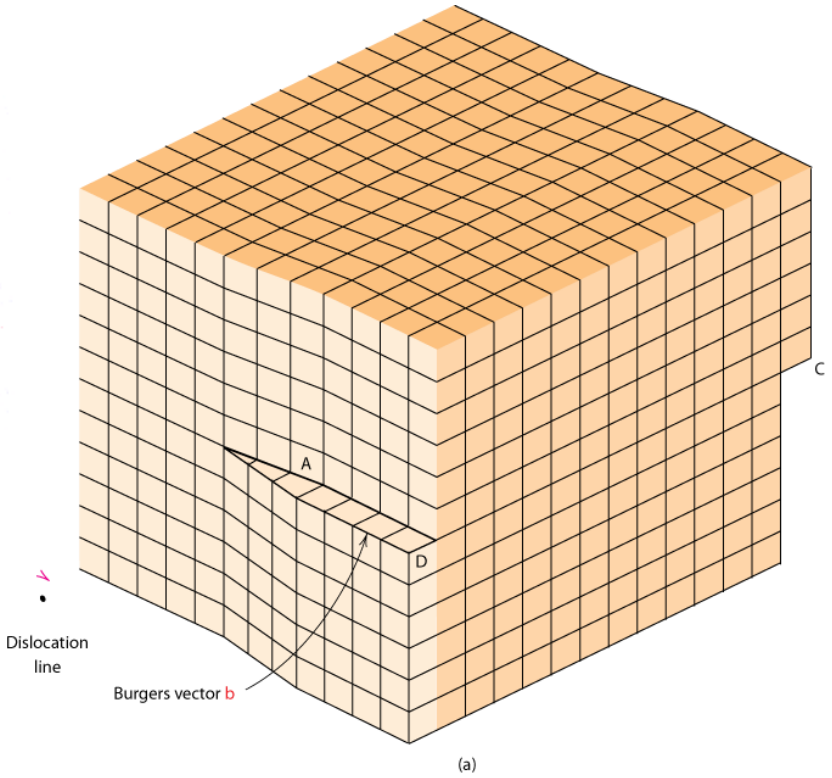
- The strength of a material with no dislocations is 20-100 times greater than the strength of a material with a high dislocation density.
- So, materials with no dislocations may be very strong, but they cannot be deformed.
- The dislocations weaken a material, but make plastic deformation possible.

Imperfections in Solids

Screw dislocation:

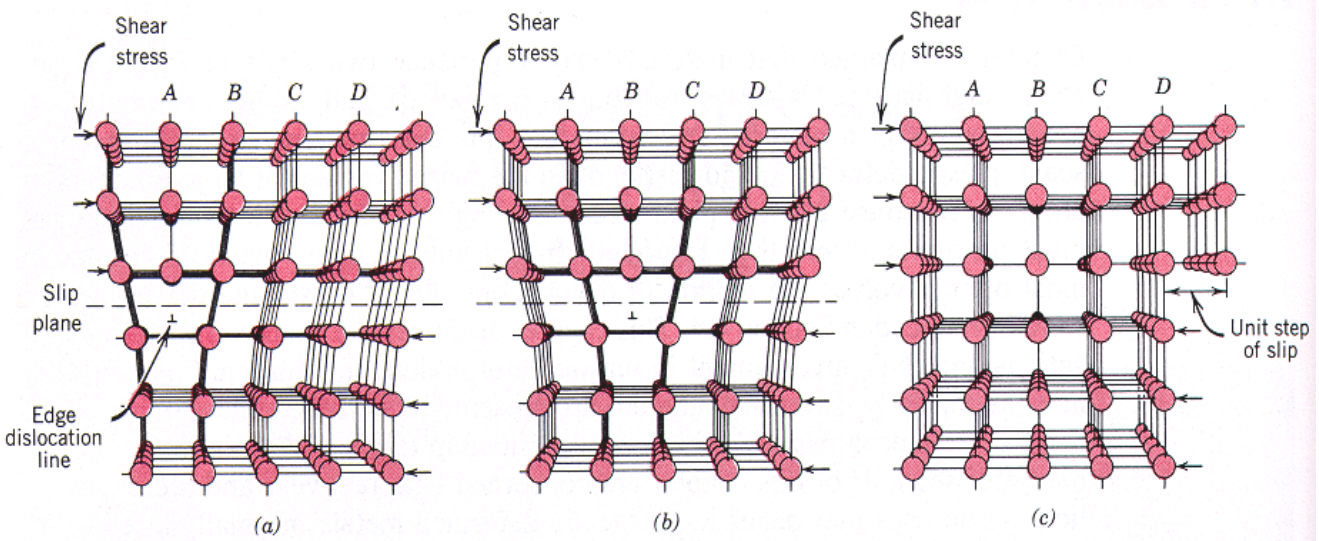
- Named for the spiral stacking of crystal planes around the dislocation line; results from **shear deformation**
- **b** parallel (||) to dislocation line

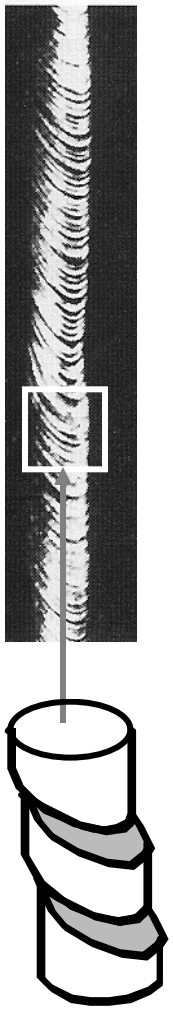




Dislocation Motion

- Produces plastic deformation,
- Depends on incrementally breaking bonds.





Plastically stretched zinc single crystal.

- If dislocations don't move, deformation doesn't happen!

Characteristics of Dislocations

- During plastic deformation, the number of dislocations increase dramatically to densities of 10^{10} mm^{-2}.
- Grain boundaries, internal defects and surface irregularities serve as formation sites for dislocations during deformation.

Dislocations During Cold Working

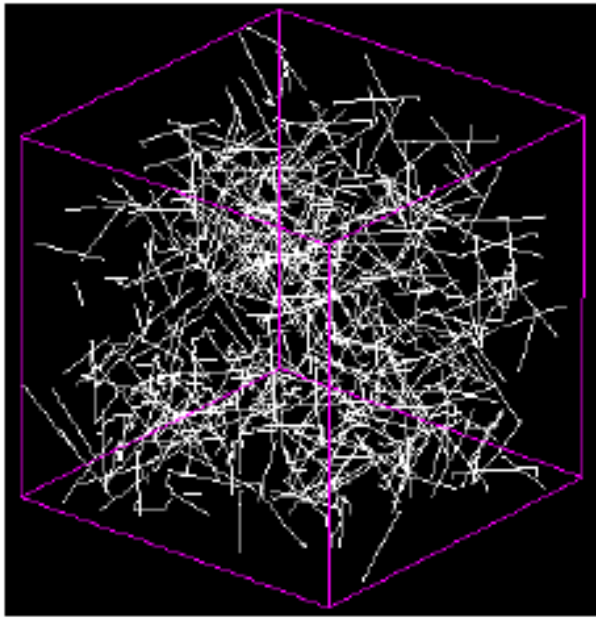
- Ti alloy after cold working.
- Dislocations entangle with one another during cold work.
- Dislocation movement becomes more difficult.
- Dislocations are visible in electron micrographs

Where do Dislocations Come From ?

The number of dislocations in a material is expressed as the **dislocation density** - the total dislocation length per unit volume or the number of dislocations intersecting a unit area. Dislocation densities can vary from 10^5 cm^{-2} in carefully solidified metal crystals to 10^{12} cm^{-2} in heavily deformed metals.

Most crystalline materials, especially metals, have dislocations in their as-formed state, mainly as a result of stresses (mechanical, thermal...) associated with the forming process.

The number of dislocations increases dramatically during plastic deformation. Dislocations spawn from existing dislocations, grain boundaries and surfaces.



This picture is a snapshot from simulation of plastic deformation in a fcc single crystal (Cu) of linear dimension 15 micrometers.

Types of Imperfections

- Vacancy atoms
- Interstitial atoms
- Substitutional atoms

Point defects
1-2 atoms

- Dislocations

Line defects
1-dimensional

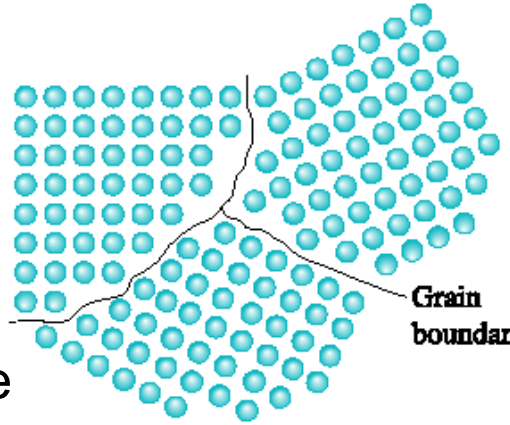
- Grain Boundaries

Area defects
2-dimensional

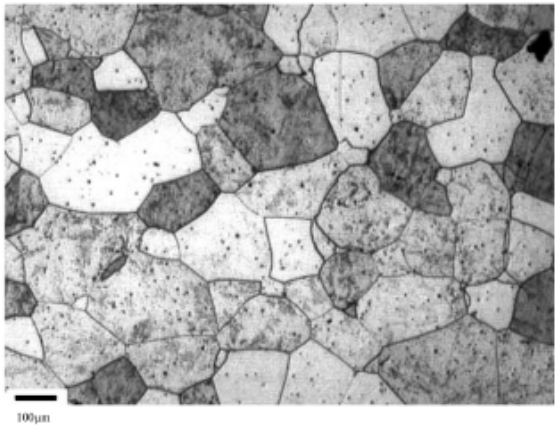
Polycrystalline Materials

Grain Boundaries

- regions between crystals
- transition from lattice of one region to another



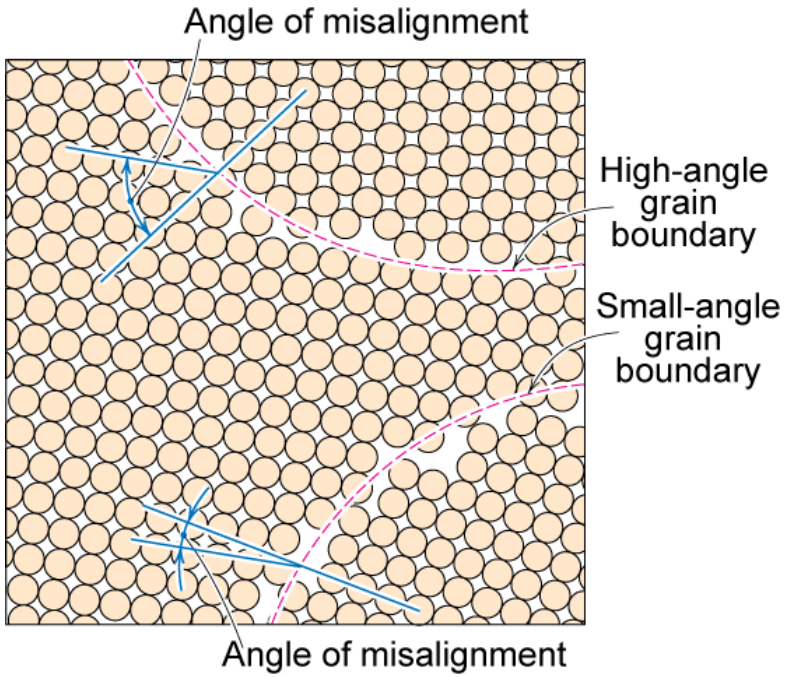
(a)



(b)

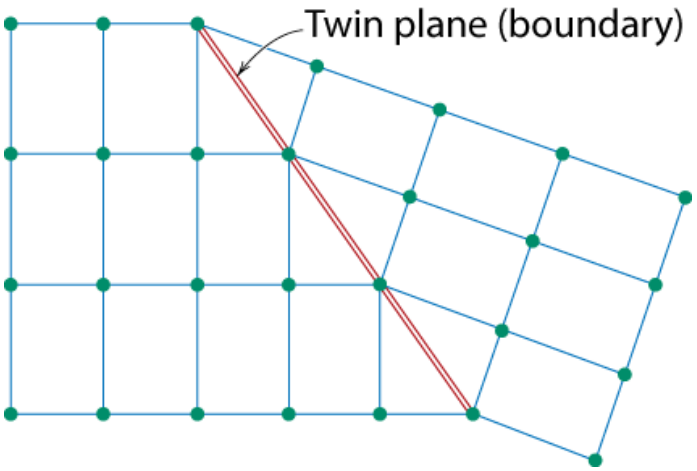
(a) The atoms near the boundaries of the 3 grains do not have an equilibrium spacing or arrangement; slightly disordered.

(b) Grains and grain boundaries in a stainless steel sample. low density in grain boundaries

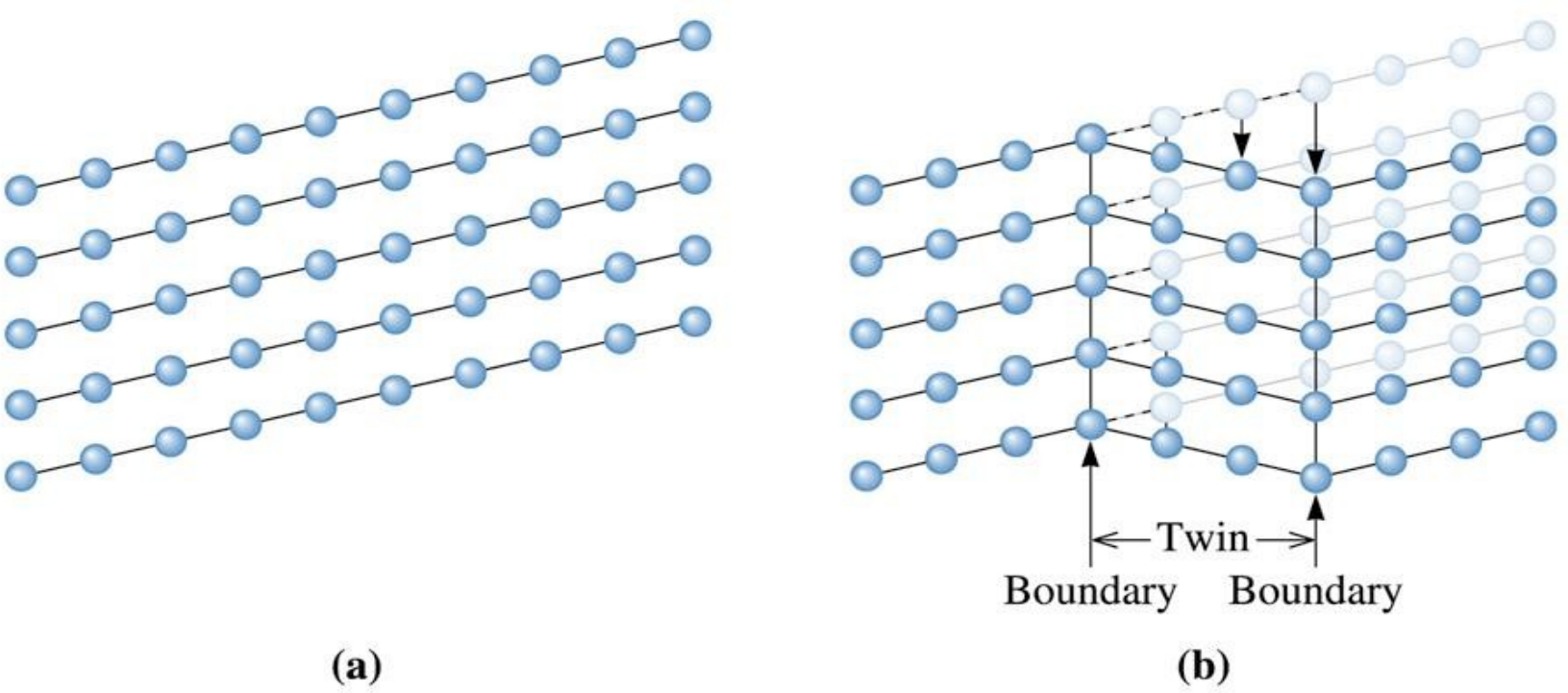


Planar Defects in Solids - Twinning

- A shear force that causes atomic displacements such that the atoms on one side of a plane (twin boundary) mirror the atoms on the other side. A reflection of atom positions across the twin plane.
- Displacement magnitude in the twin region is proportional to the atom's distance from the twin plane.
- Takes place along defined planes and directions depending upon the system.
    - Ex: BCC twinning occurs on the (112)[111] system



Twinning

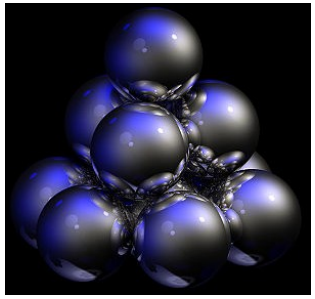


Applied stress to a perfect crystal (a) may cause a displacement of the atoms, (b) causing the formation of a twin. Note that the crystal has deformed as a result of twinning.

- Stacking faults
  - For FCC metals an error in ABCABC packing sequence
  - Ex: ABCABABC

Properties of Twinning

- Of the three common crystal structures BCC, FCC and HCP, the HCP structure is the most likely to twin.
- FCC structures will not usually twin because slip is more energetically favorable.
- Twinning occurs at low temperatures and high rates of shear loading (shock loading) conditions where there are few present slip systems (restricting the possibility of slip)
- Small amount of deformation when compared with slip.



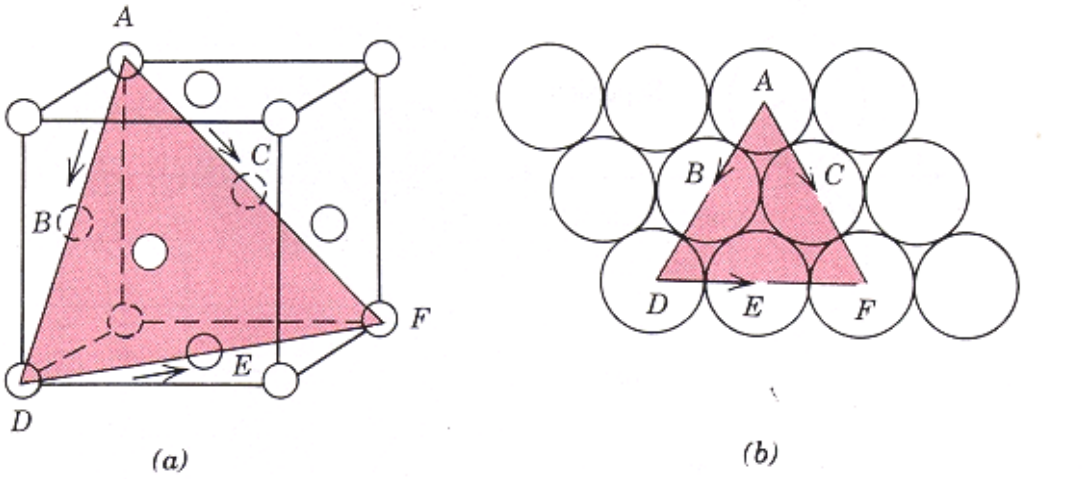
Comparison

Slip	Twinning
orientation of atoms remains the same	reorientation of atomic direction across twin plane
displacements take place in exact atomic spacings	atomic displacement is less than interatomic spacing

Slip Systems

- Usually there are preferred slip planes and directions in crystal systems.
- The combination of both the slip plane and direction form the slip system.
  - Slip plane is generally taken as the closest packed plane in the system
  - Slip direction is taken as the direction on the slip plane with the highest linear density.

Slip systems



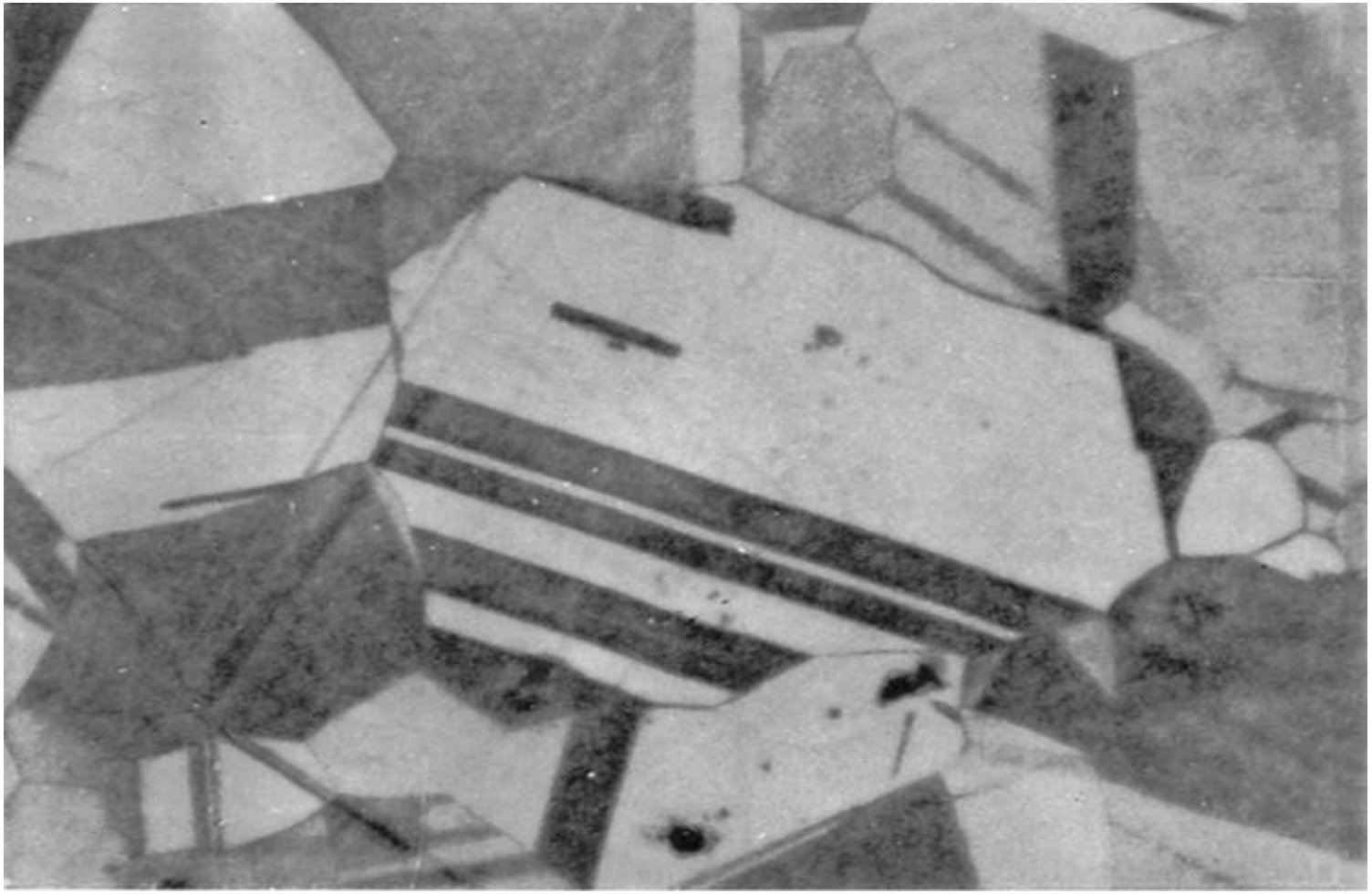
(*a*) A {111}⟨110⟩ slip system shown within an FCC unit cell. (*b*) The (111) plane from (*a*) and three ⟨110⟩ slip directions (as indicated by arrows) within that plane comprise possible slip systems.

- FCC and BCC materials have large numbers of slip systems (at least 12) and are considered ductile.
- HCP systems have few slip systems and are quite brittle.

Slip systems

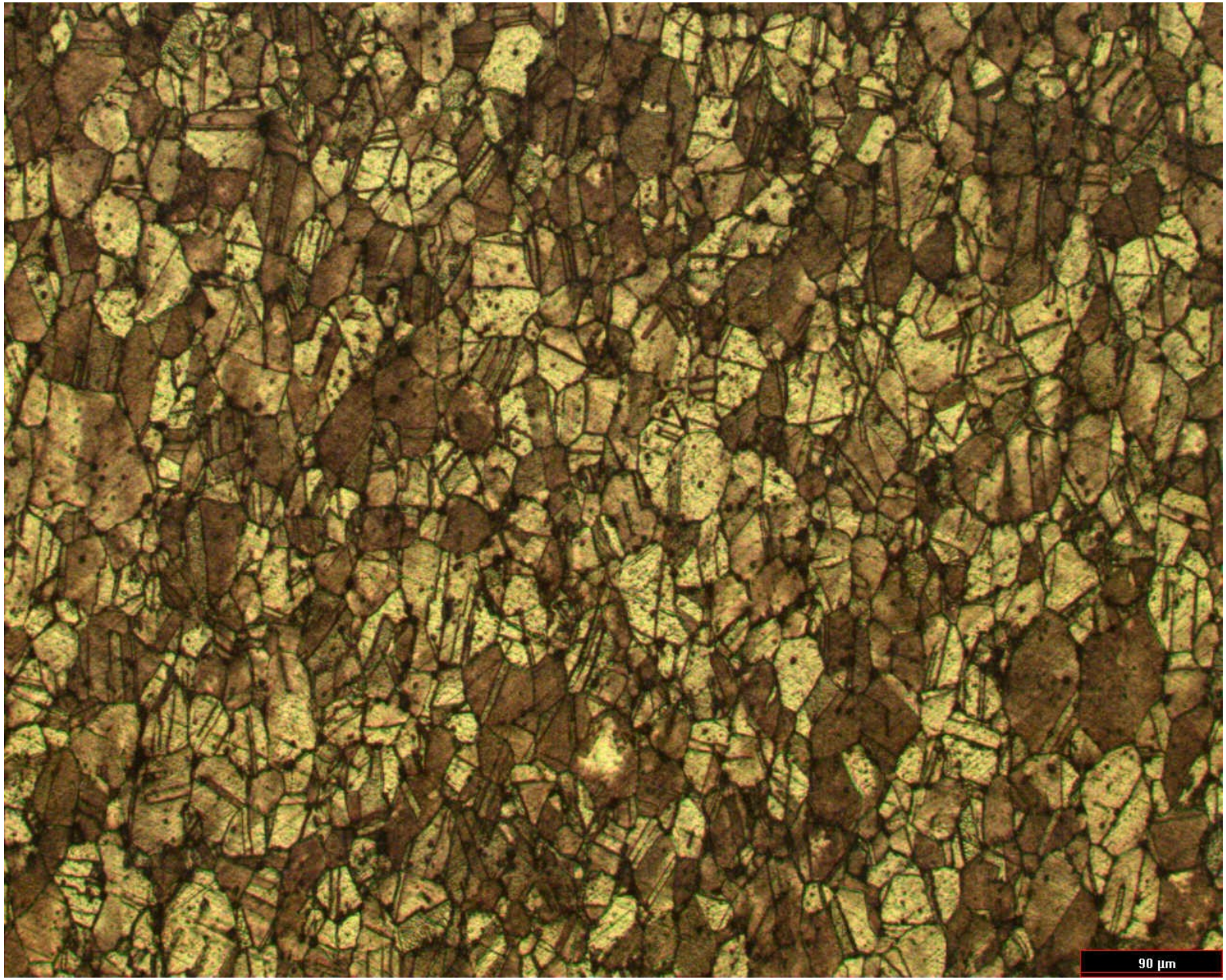
Factor	FCC	BCC	HCP $\left(\frac{c}{a} > 1.633\right)$
Critical resolved shear stress (psi)	50–100	5,000–10,000	50–100[a]
Number of slip systems	12	48	3[b]
Cross-slip	Can occur	Can occur	Cannot occur[b]
Summary of properties	Ductile	Strong	Relatively brittle

[a] *For slip on basal planes.*
[b] *By alloying or heating to elevated temperatures, additional slip systems are active in HCP metals, permitting cross-slip to occur and thereby improving ductility.*



A micrograph of twins within a grain of brass (x250).

Brass (90 micron scale bar)

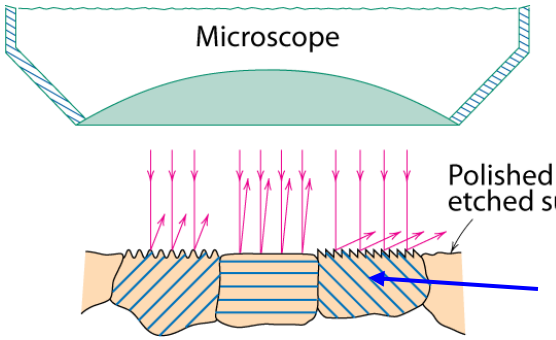


Microscopic Examination

- Metallography – sample preparation is necessary to examine the surface of materials (metals, ceramics, polymers).
- A smooth mirror-like finish is obtained by grinding and polishing using successively finer abrasive papers and powder mixed with water.
- The microstructure (grain size, shape, orientation) is revealed using a chemical reagent (etching solution) on a polycrystalline sample.
- Etching characteristics vary from grain to grain.

Optical Microscopy

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



Micrograph of brass (a Cu-Zn alloy)

Optical Microscopy

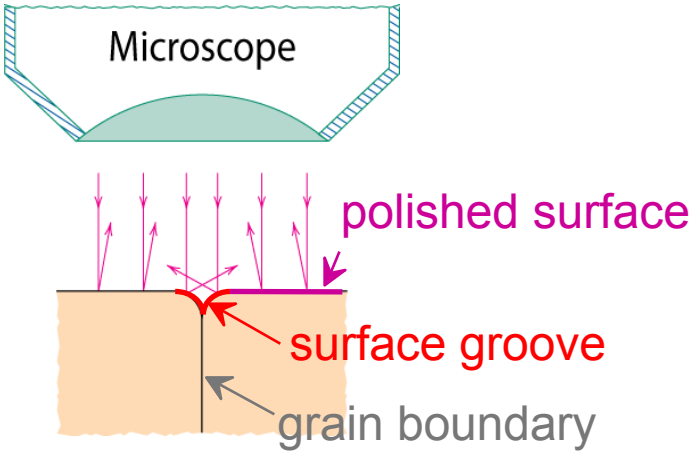
Grain boundaries...

- are imperfections,
- are more susceptible to etching,
- may be revealed as dark lines,
- change in crystal orientation across boundary.

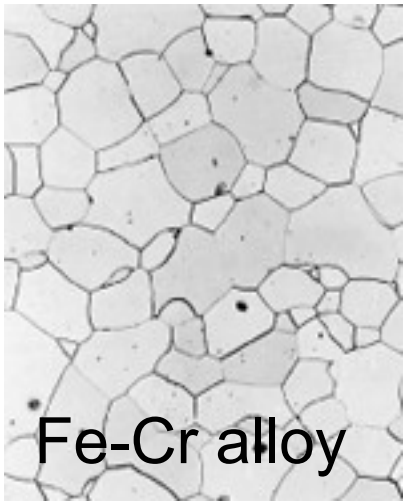
ASTM grain size number

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

number of grains/in^2 at 100x magnification



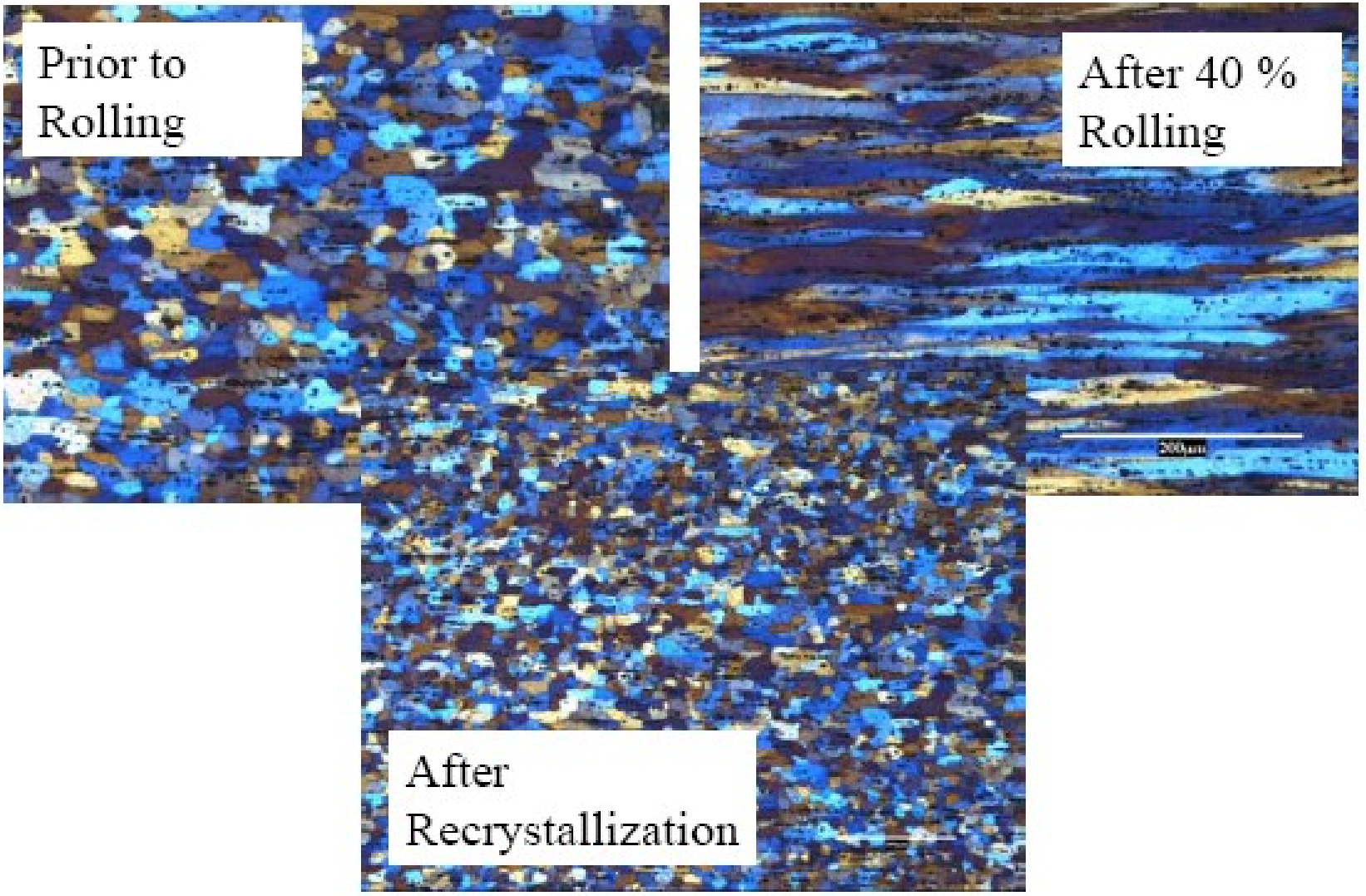
(a)



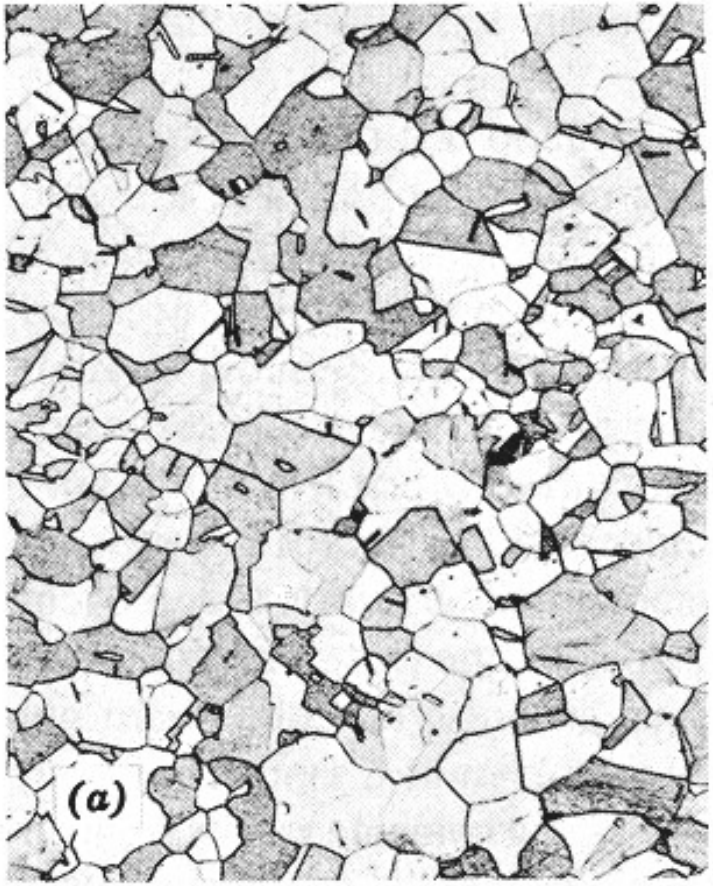
(b)

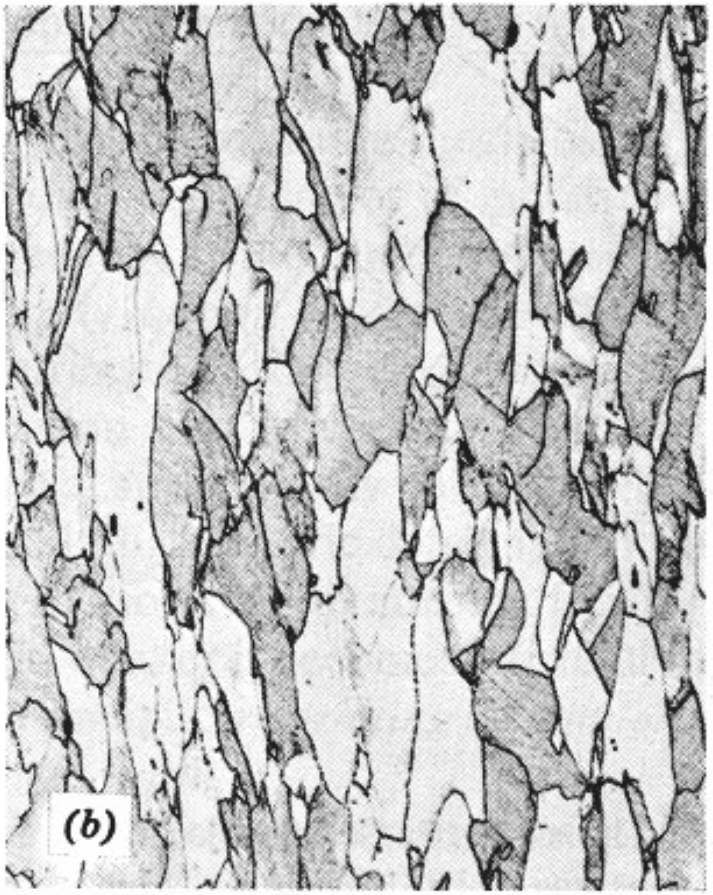
Adapted from Fig. 5.19(a) and (b), *Callister & Rethwisch 3e.* (Fig. 5.19(b) is courtesy of L.C. Smith and C. Brady, the National Bureau of Standards, Washington, DC [now the National Institute of Standards and Technology, Gaithersburg, MD].)

Change in Microstructure due to Cold Work



Polycrystalline Deformation



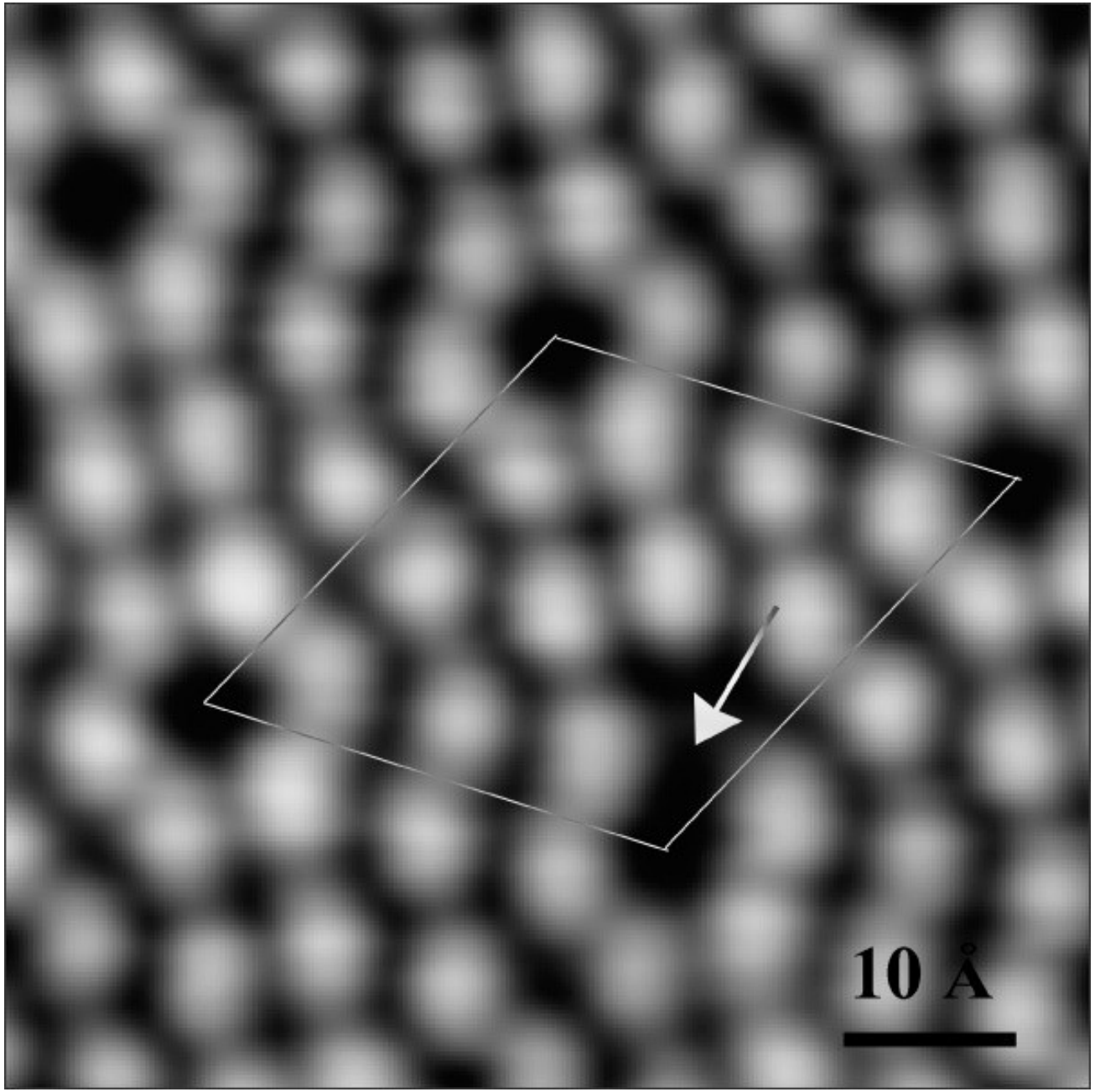


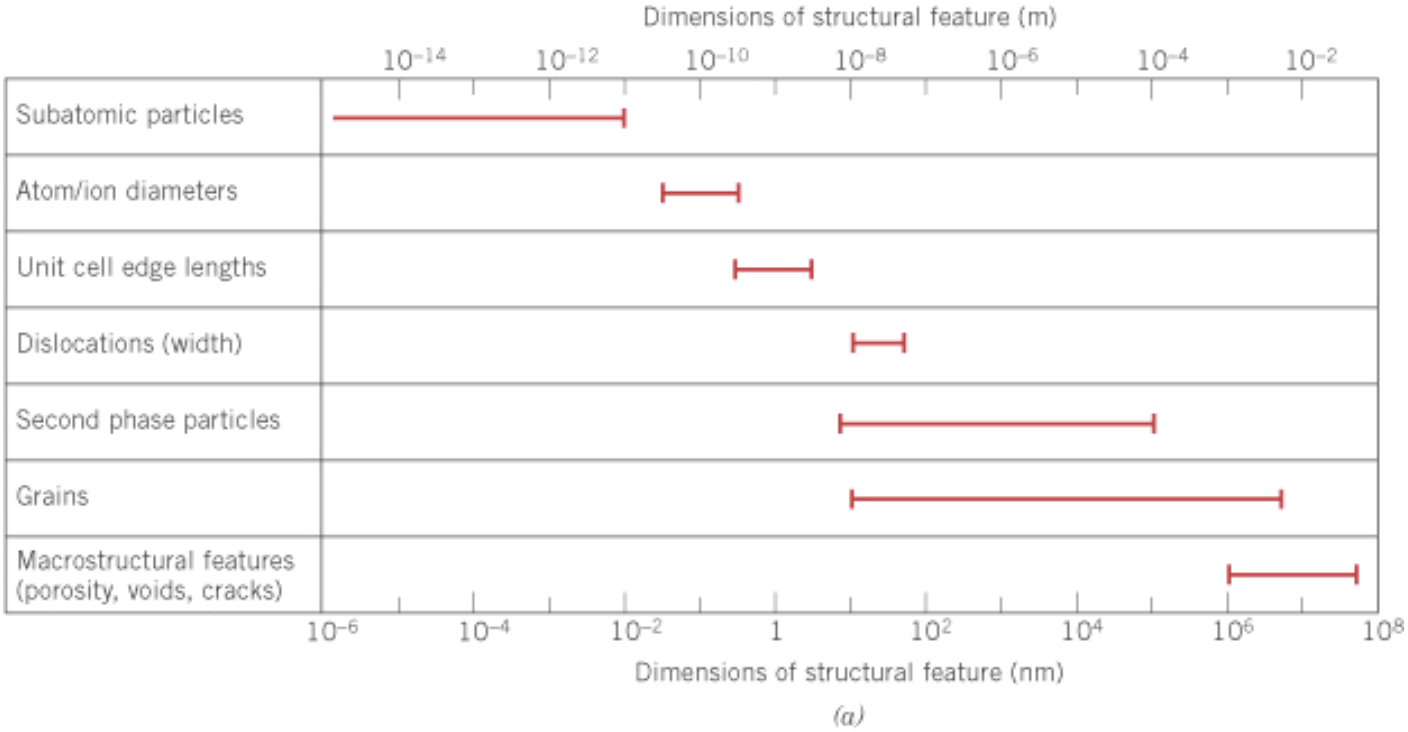
Microscopy

Optical (light) resolution (0.1 μm = 100 nm = 10^{-7} m)

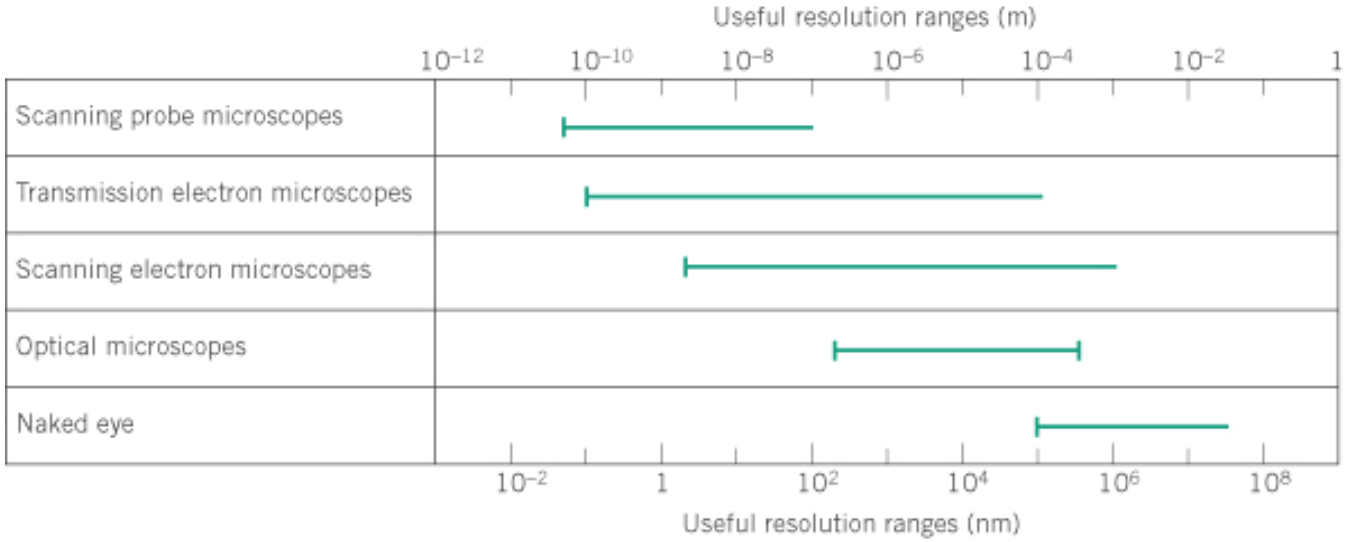
For higher resolution need higher frequency

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


10 Å


Dimensions of structural feature (m)
10⁻¹⁴
10⁻¹²
10⁻¹⁰
10⁻⁸
10⁻⁶
10⁻⁴
10⁻²
Subatomic particles
Atom/ion diameters
Unit cell edge lengths
Dislocations (width)
Second phase particles
Grains
Macrostructural features (porosity, voids, cracks)
10⁻⁶
10⁻⁴
10⁻²
1
10²
10⁴
10⁶
10⁸
Dimensions of structural feature (nm)

(a)


Useful resolution ranges (m)
10⁻¹²
10⁻¹⁰
10⁻⁸
10⁻⁶
10⁻⁴
10⁻²
1
Scanning probe microscopes
Transmission electron microscopes
Scanning electron microscopes
Optical microscopes
Naked eye
10⁻²
1
10²
10⁴
10⁶
10⁸
Useful resolution ranges (nm)

(b)