Introduction to Materials Science and Engineering

Chapter 4. Defects in Solids

- What types of defects arise in solids?
- Can the number and type of defects be varied and controlled?
- How do defects affect the material properties?
- Are defects undesirable? *(그때 그때 달라요)*

Contents

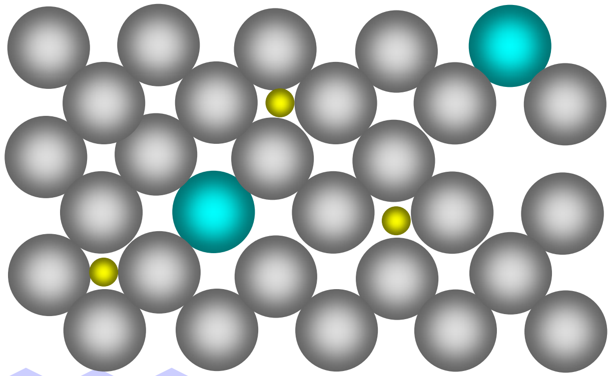
Introduction

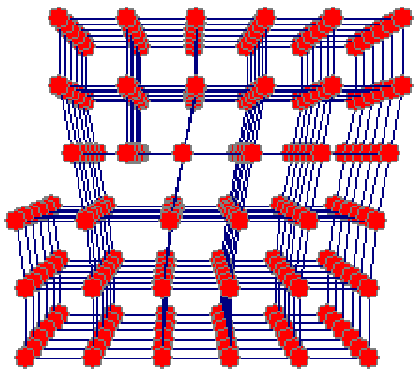
- Perfect and extensive ordering may not exist.
- Crystalline imperfections have a profound effect on the materials behavior.
- By controlling the lattice imperfections, it is possible to produce:
  - √ Stronger metals and alloys.
  - √ More powerful magnets.
  - √ Improved transistors and solar cells.
  - √ Glassware of striking colors.

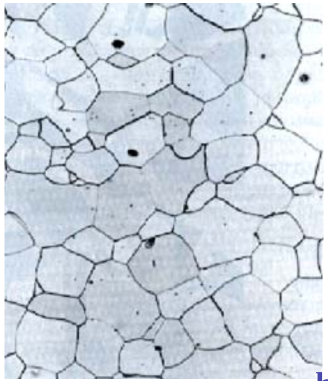
Introduction

➢ Types of Imperfections

0 dimensional	Point defects	Vacancies Interstitials (Substitutional atoms) (Interstitial atoms)
1 dimensional	Line defects	Dislocations
2 dimensional	Planar (Area) defects	Surface Grain boundary Stacking fault





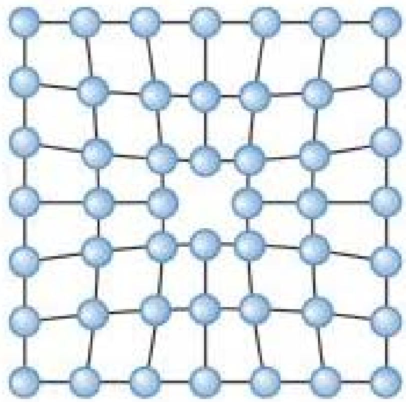


Contents

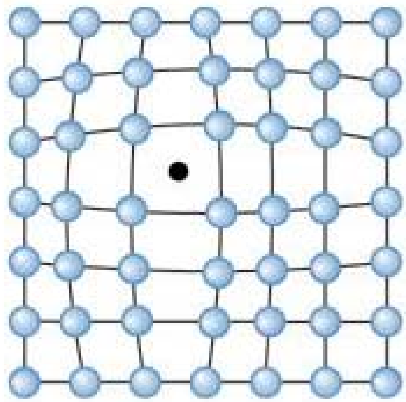
Point Defects

- Point defects - Imperfections, such as vacancies, that are located typically at site(s) in the crystal.
- Vacancy - An atom or an ion missing from its regular crystallographic site.
- Interstitial - A point defect produced when an atom is placed into the crystal at a site that is normally not a lattice point.
- Substitutional defect - A point defect produced when an atom is removed from a regular lattice point, and replaced by a different atom.

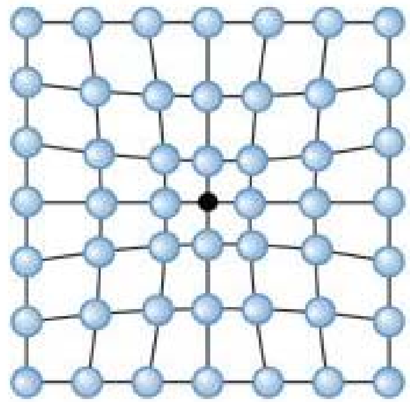
Point Defects



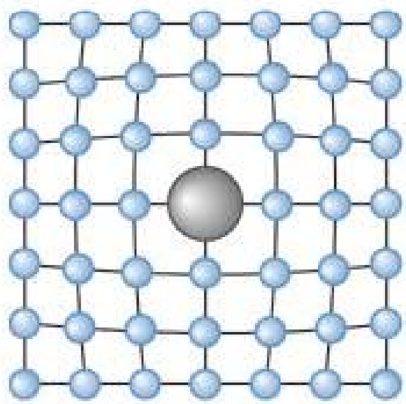
vacancy



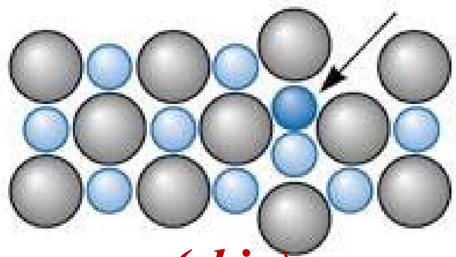
interstitial atom



small substitutional atom



large substitutional atom



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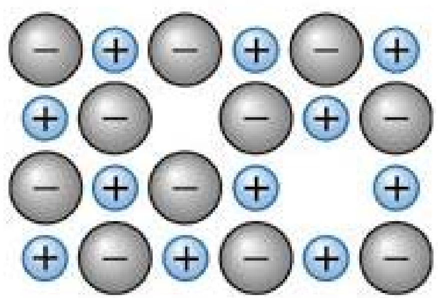
Frenkel defect

(e)



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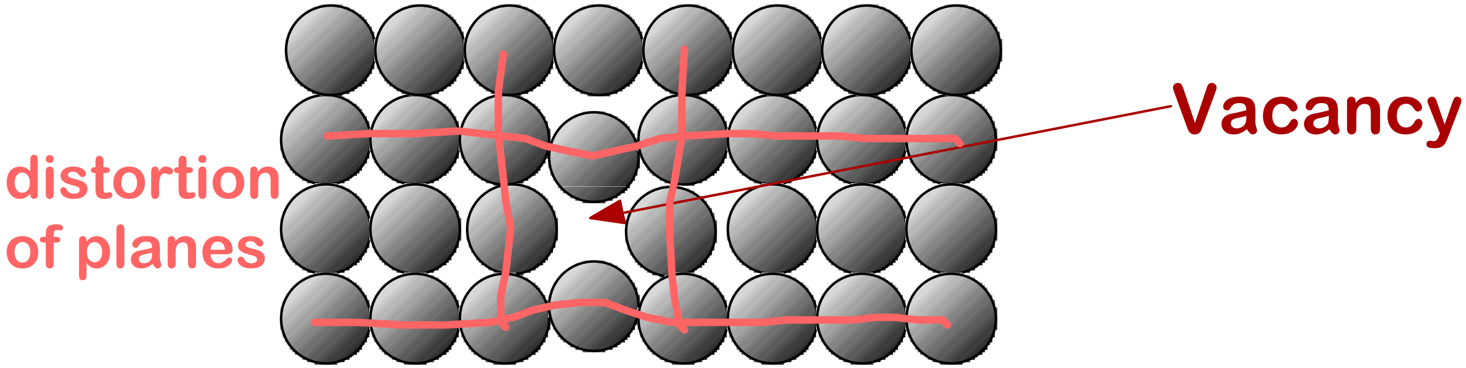
Schottky defect

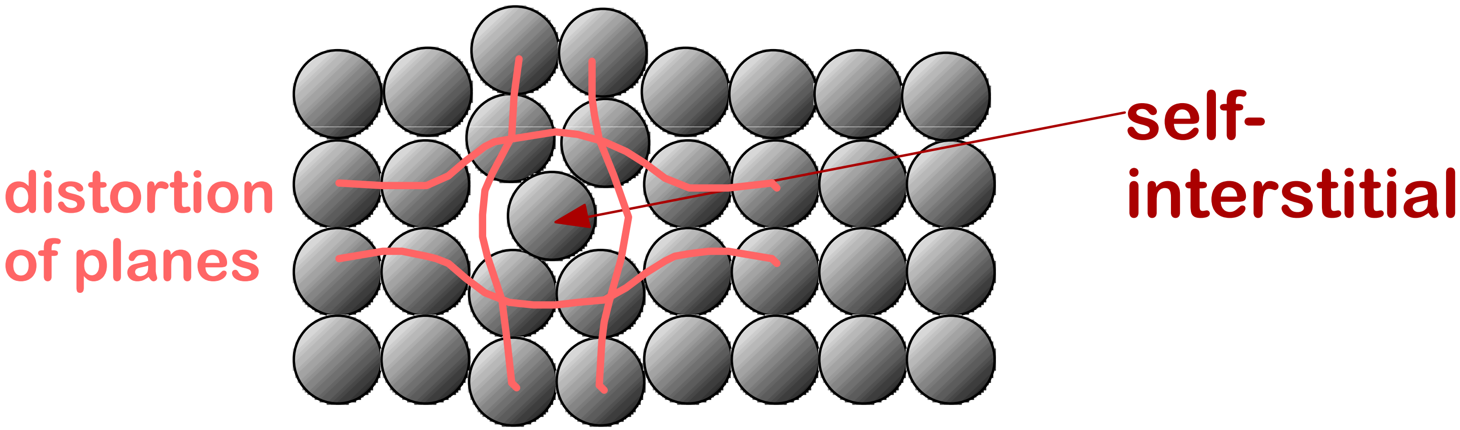
All of these defects disrupt the perfect arrangement of the surrounding atoms.

Point Defects

- **Vacancies:** vacant atomic sites in a structure

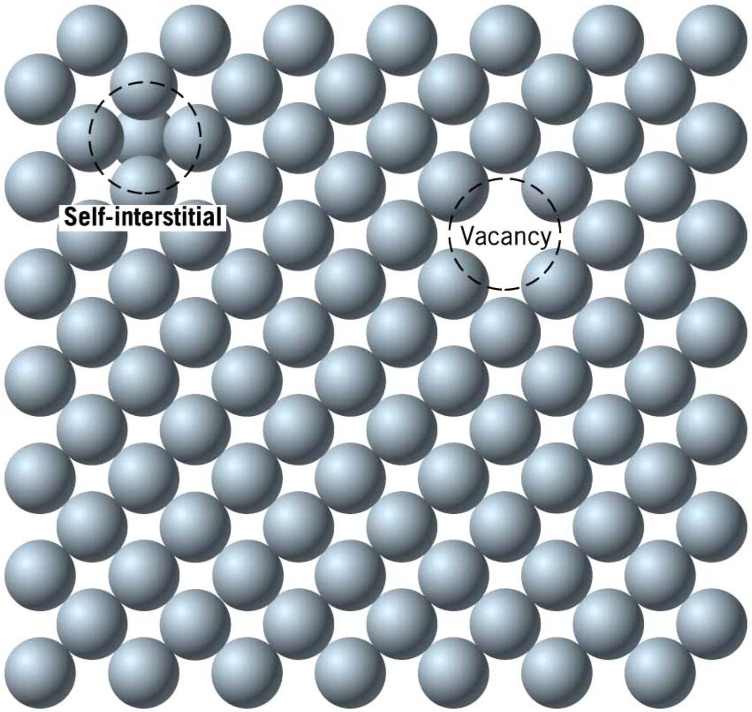


- **Self-Interstitials:** "extra" atoms positioned between atomic sites

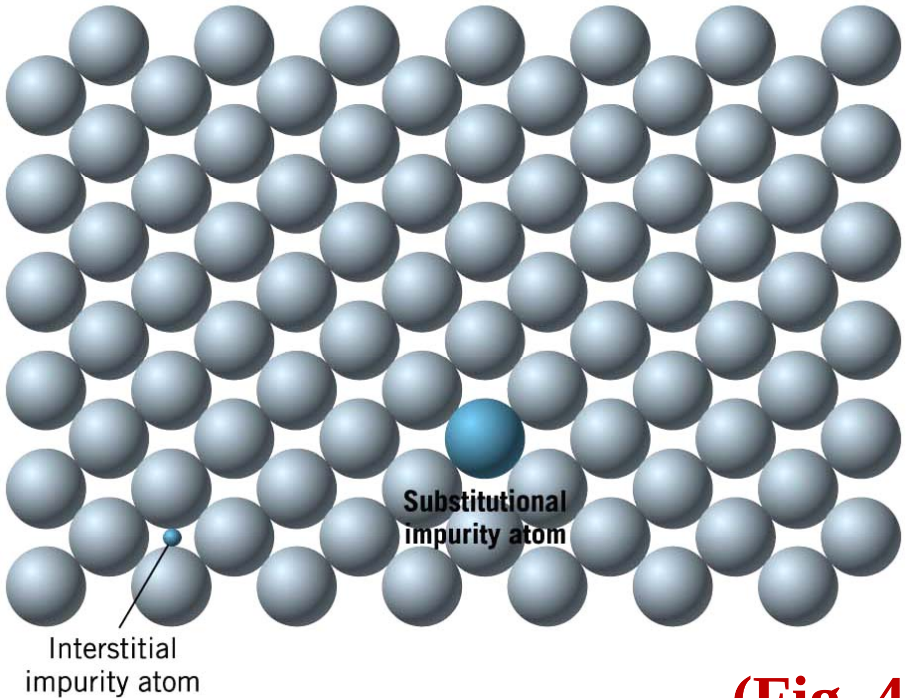


Point Defects

- vacancy vs. interstitial
- <u>solute = impurity</u> *(substitutional or interstitial)*



(Fig. 4-1)



(Fig. 4-2)

The value of seeing nothing

Jochen Mannhart and Darrell G. Schlom

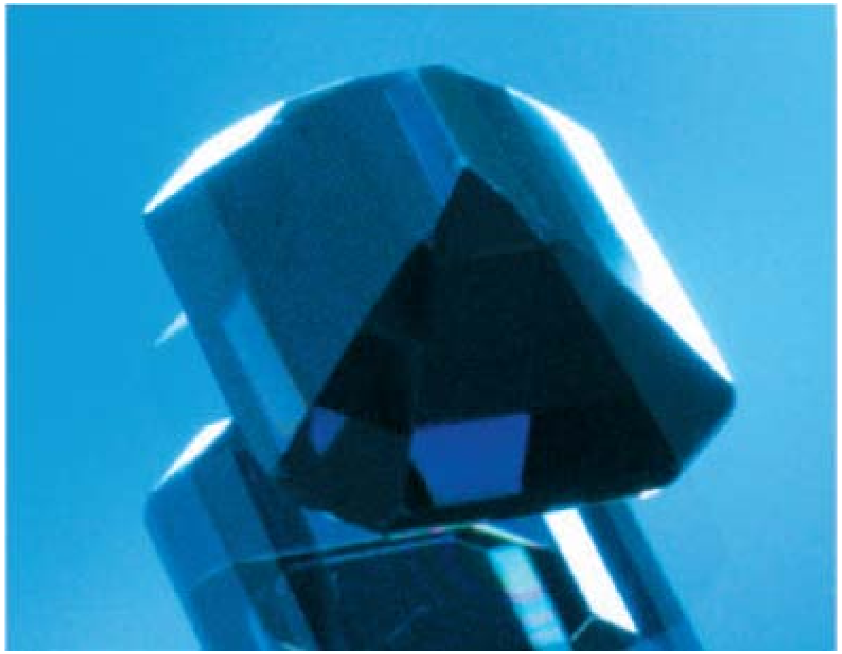


Figure 1 Now you see it, now you don't. These micrographs of a $SrTiO_3$ crystal show the effect of removing oxygen atoms, leaving vacancies in the crystal lattice: the glistening oxidized gem (top) is transformed into a dull blue, conductive crystal (bottom).

Oxygen vacancy V_o + 2e'

Thermodynamics of Point Defects

- Gibbs free energy $G = H - TS$

  H : enthalpy, S : entropy

- Point defects → break bonds

  → increase internal energy (strain energy) → H ↑

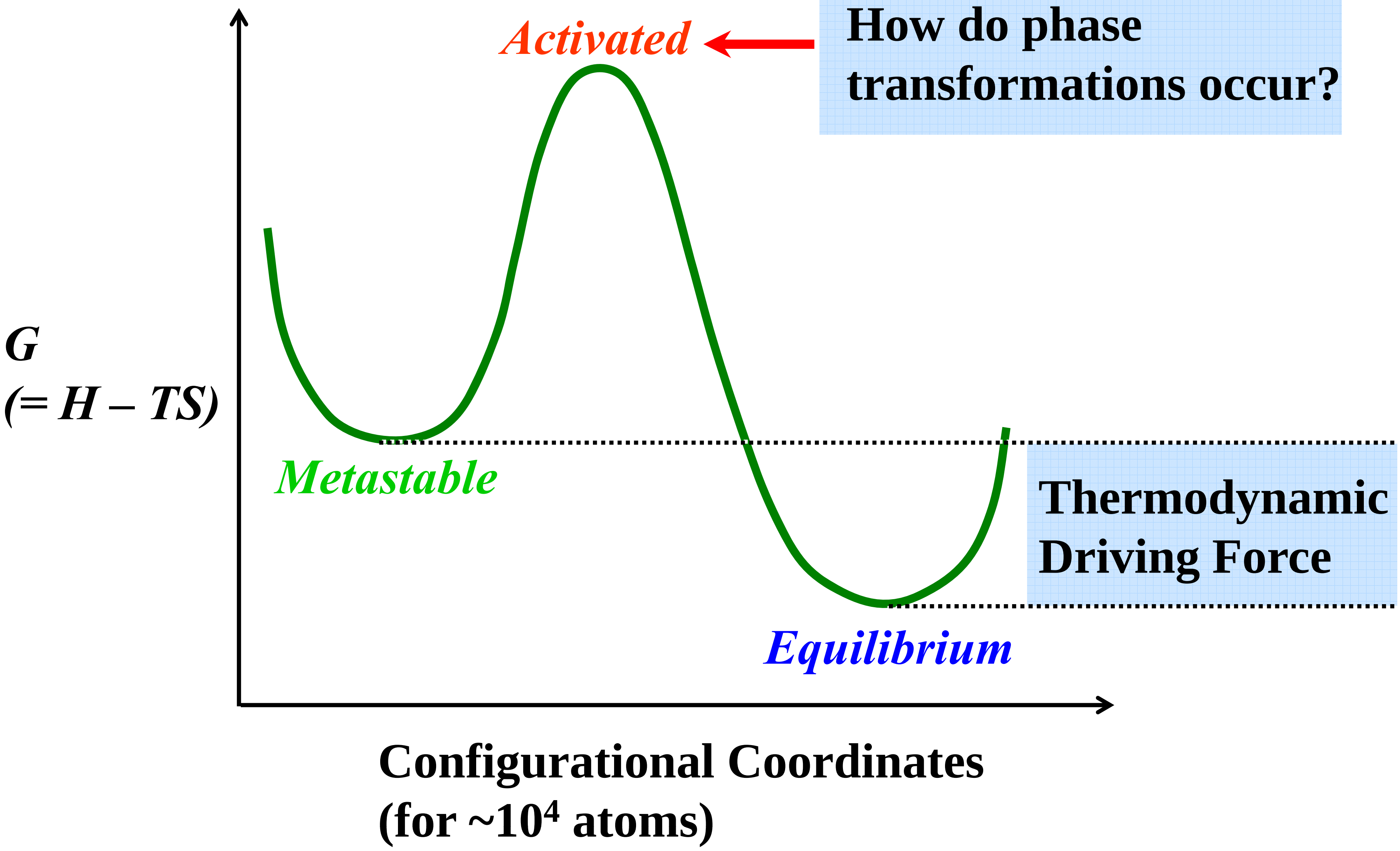
Point defects → increase distinct possible arrangements of atoms → S ↑

⇒ Proper point defects thermodynamically perfect

➢ Thermodynamic arguments suggest that point defects should be present at a finite temperature.

➢ It is impossible to create a stable single crystal without point defects at a finite temperature.

How do phase transformations occur?



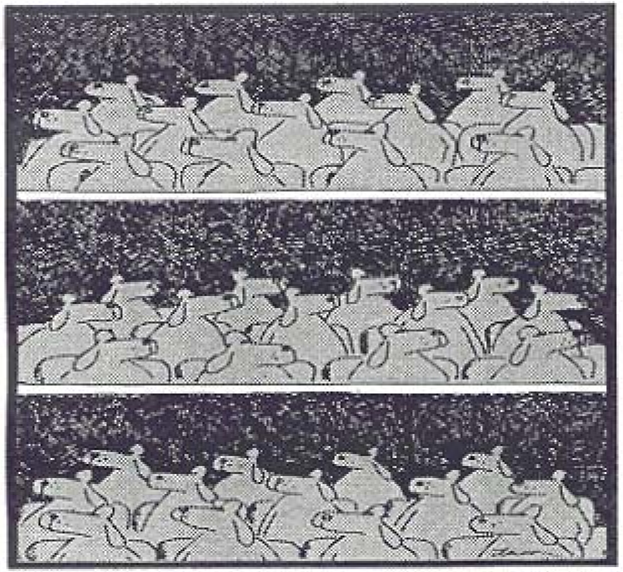
$$G \equiv H - TS$$

Low Temperature

Enthalpy

High Temperature

Entropy



At the popular dog film, *Man Throwing Sticks*

Point Defects ??

➢ Equilibrium concentration varies with temperature!

How does the vacancy concentration depend on temp.?

No. of defects

Activation energy

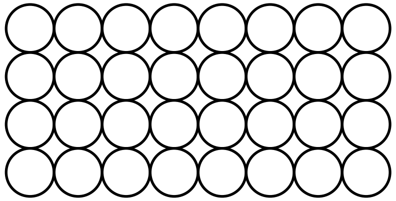
$$\frac{N_D}{N} = \exp\left(\frac{-Q_D}{k_B T}\right)$$

No. of potential defect sites.

Temperature

Boltzmann's constant

$k_B = 8.617 \times 10^{-5}$ eV/atom•K



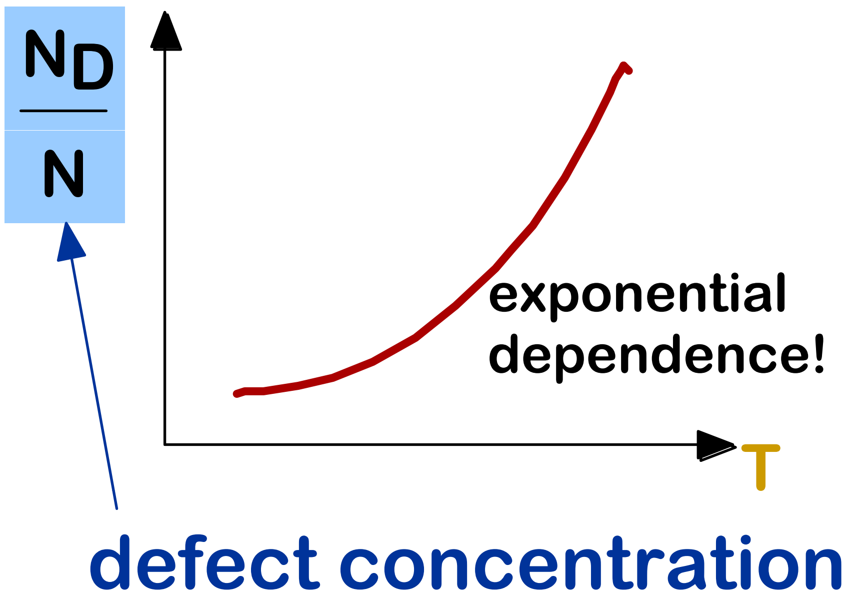
Each lattice site is a potential vacancy site

Point Defects

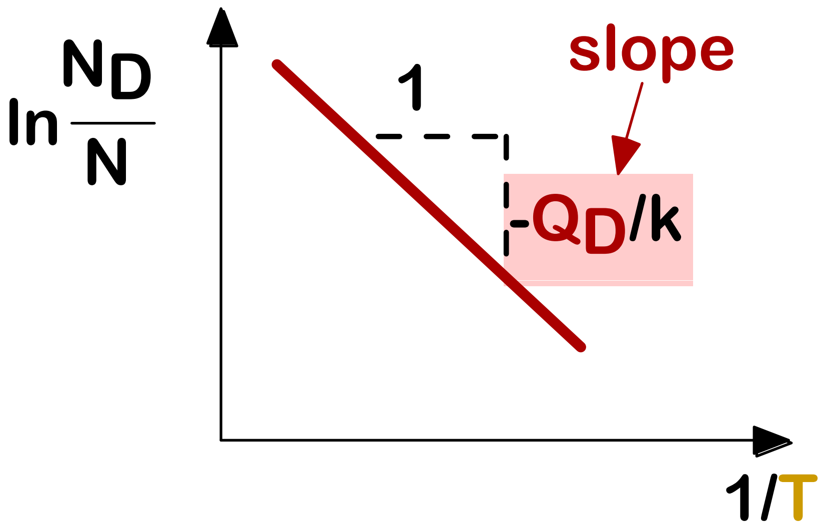
MEASURING ACTIVATION ENERGY

- We can get Q_D from an experiment $\frac{N_D}{N} = \exp\left(\frac{-Q_D}{kT}\right)$

- Measure this...

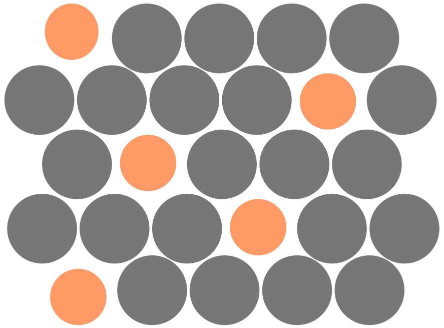


- Replot it...

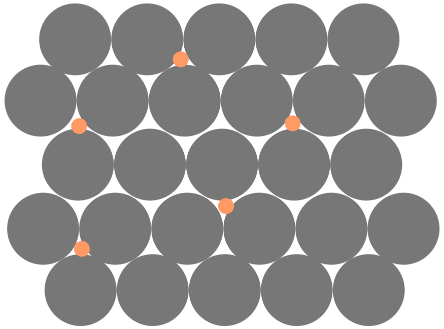


Solid Solution or Phase Separation

- Two outcomes if impurity (*B*) is added to host (*A*)
  1. Solid solution of *B* in *A* (i.e., random dist. of point defects)



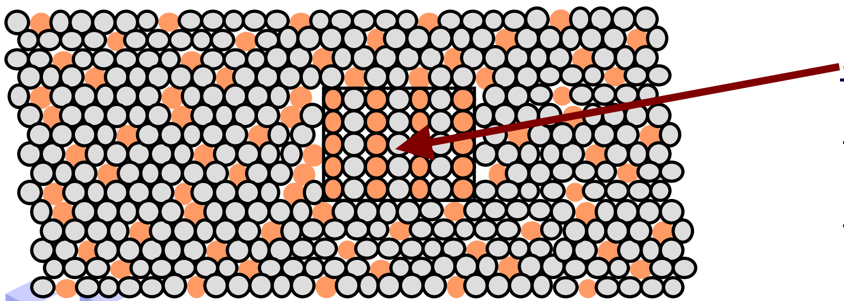
OR



Substitutional alloy (e.g., Cu in Ni)

Interstitial alloy (e.g., C in Fe)

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

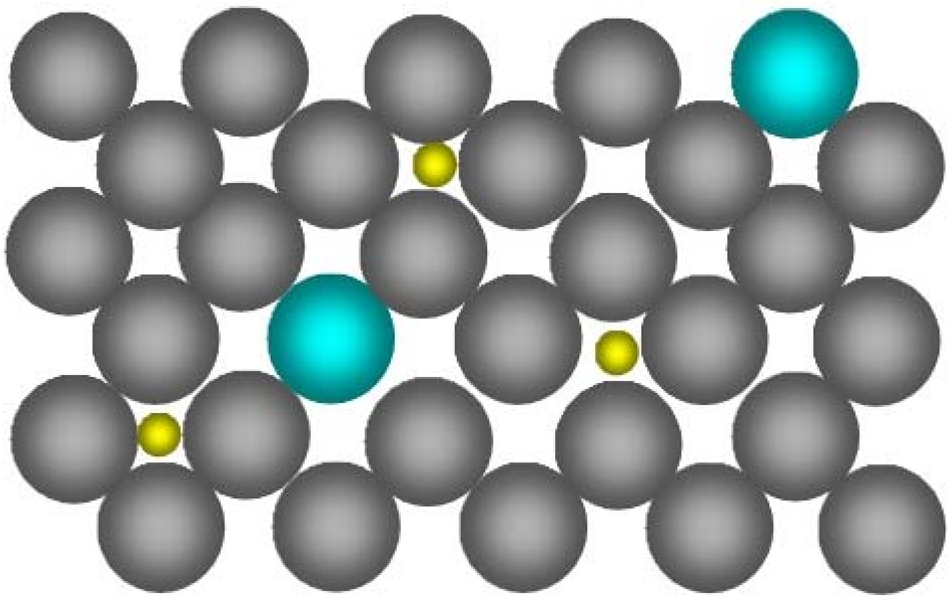


Second-phase precipitates

- different composition
- often different structure

Solid Solution

- An alloy resulting from the addition of solute atoms to the solvent.
- The crystal structure is maintained and no new structures are formed.
- A solid that consists of two or more elements atomically dispersed in a single-phase structure.



unit cell ???

Point Defects in Ionic Crystals

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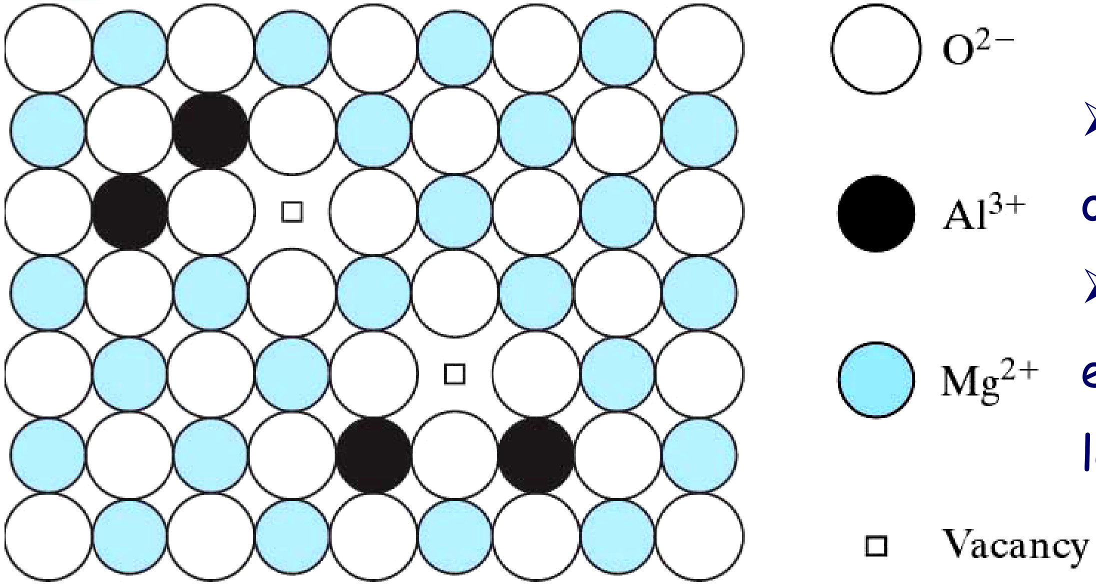
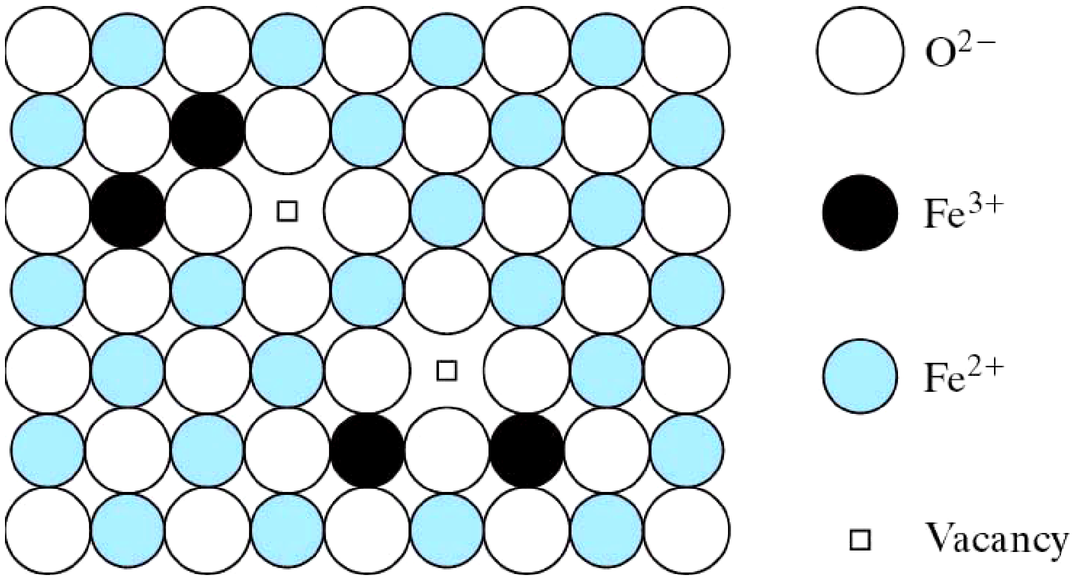


- Substitutional solid solution of Al_2O_3 in MgO
- Only two Al^{3+} ions can fill every three Mg^{2+} vacant sites, leaving one Mg^{2+} vacancy



- Non-stoichiometric compound $Fe_{1-x}O$ with x ~ 0.05
- Both Fe^{2+} and Fe^{3+} occupy cation sites, with one Fe^{2+} vacancy occurring for every two Fe^{3+} ions present

Specification of Composition

- Definition: Amount of impurity (B) and host (A) in the system
- Two descriptions:
  - **Weight %** (Eq. 4-3)

$$C_B = \frac{\text{mass of B}}{\text{total mass}} \times 100$$

  - **Atomic %** (Eq. 4-5)

$$C'_B = \frac{\text{\# atoms of B}}{\text{total \# atoms}} \times 100$$

- Conversion between wt. % and at. % in an *A-B* alloy:

- Basis for conversion:

mass of B = moles of B x A_B ← atomic weight of B

mass of A = moles of A x A_A ← atomic weight of A

Contents

Dislocations

- Dislocation - A line imperfection in a crystalline material.
- Screw dislocation - A dislocation produced by skewing a crystal so that one atomic plane produces a spiral ramp about the dislocation.
- Edge dislocation - A dislocation introduced into the crystal by adding an "extra half plane" of atoms.
- Mixed dislocation - A dislocation that contains partly edge components and partly screw components.
- Slip - Deformation of a metallic material by the movement of dislocations through the crystal.

Some Fundamental Questions related to the Mechanical Properties

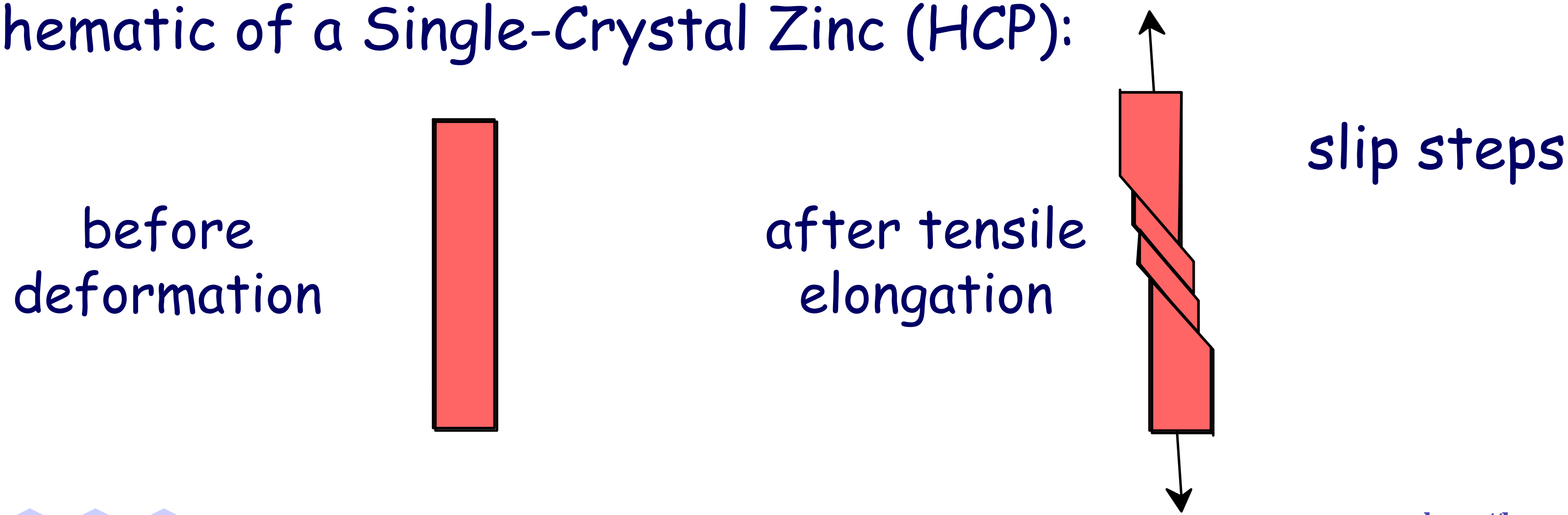
- Why are ceramics brittle and metals not?
- Why do metals bend instead of being broken?
- What happens to the atomic arrangements in the elastically and plastically deformed metals?

Dislocation

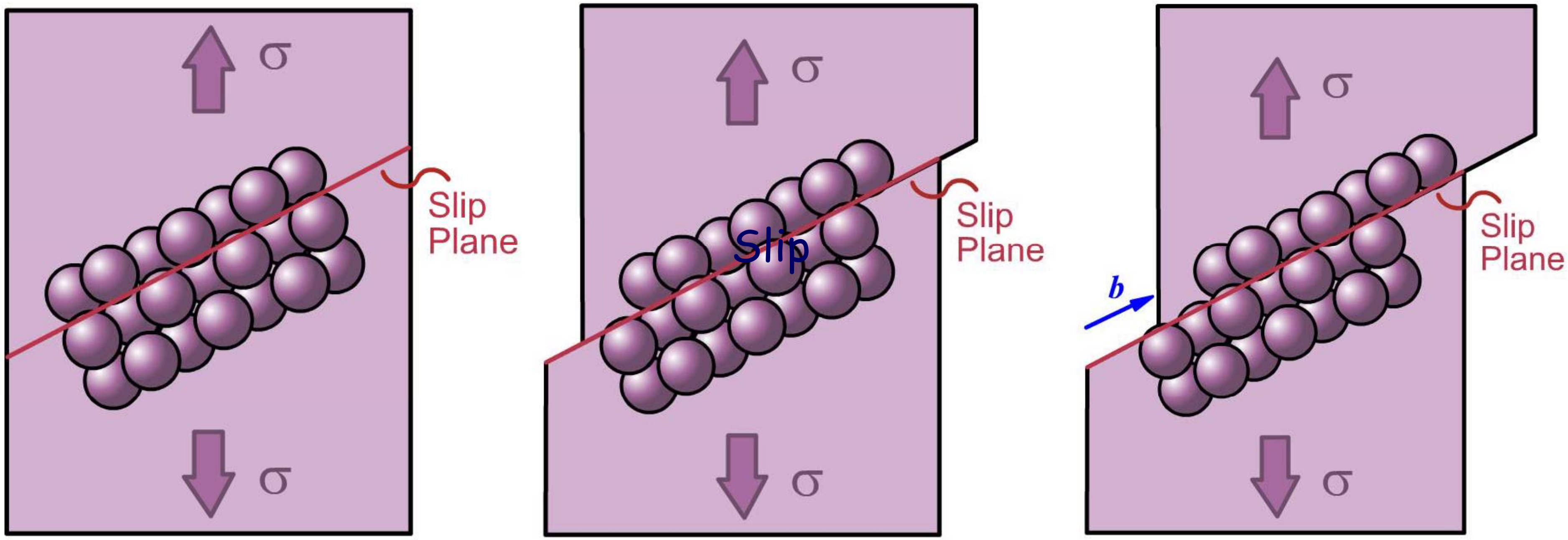
Dislocations:

- ✓ Line defects
- ✓ Cause slip between crystal planes when they move
- ✓ Produce permanent (plastic) deformation.

Schematic of a Single-Crystal Zinc (HCP):



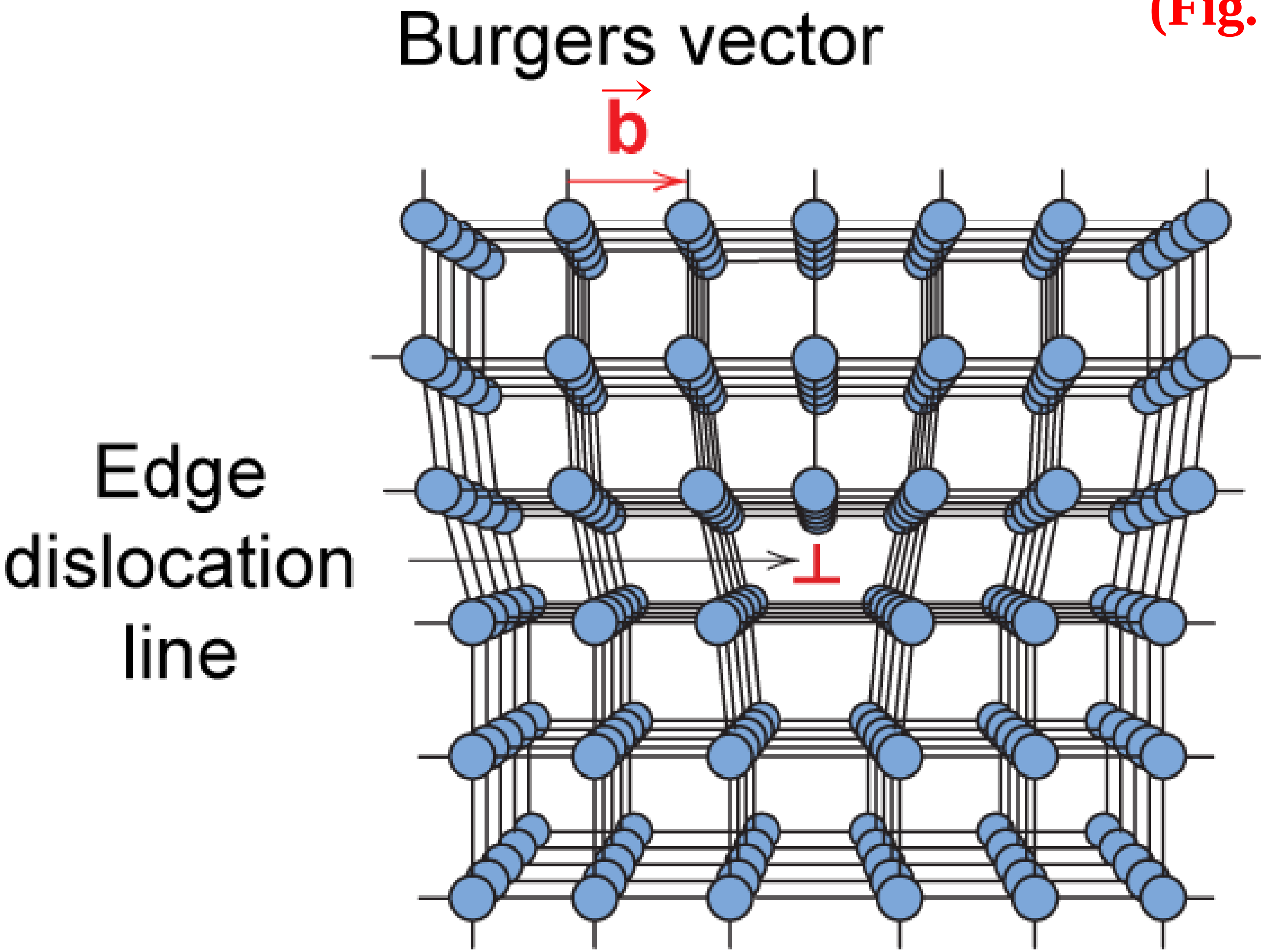
Slip



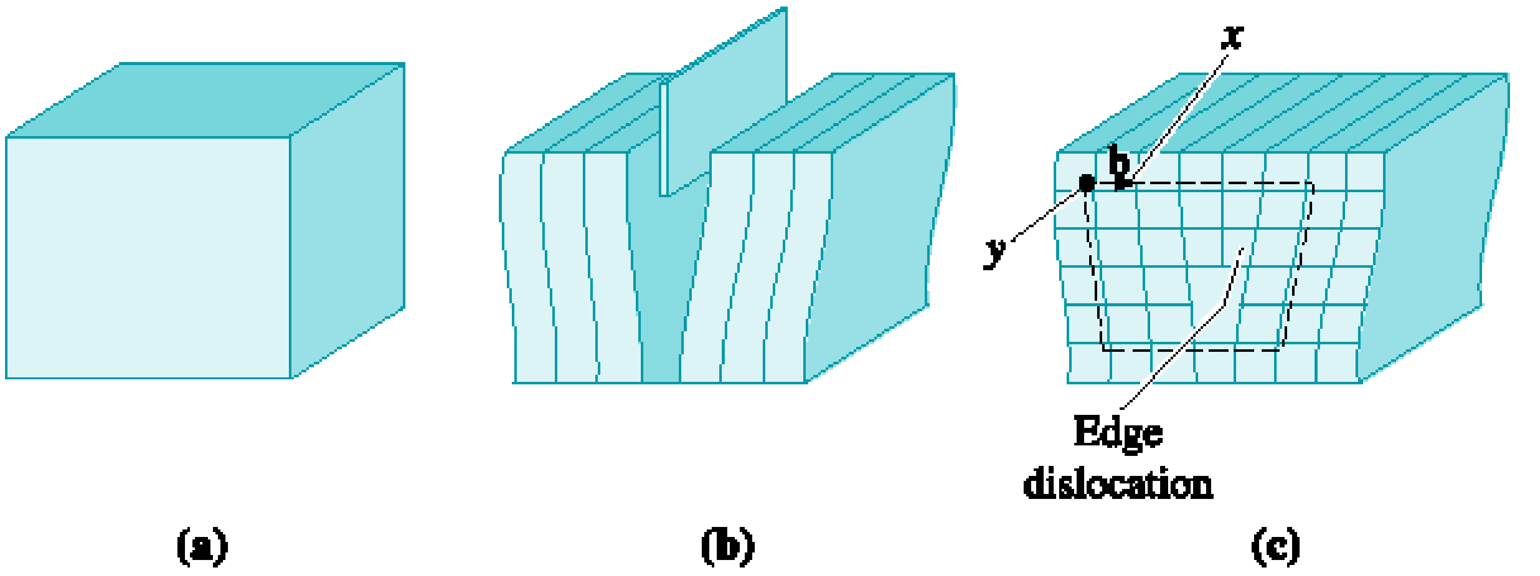
Dislocation

➢ Edge Dislocation

(Fig. 4-3)



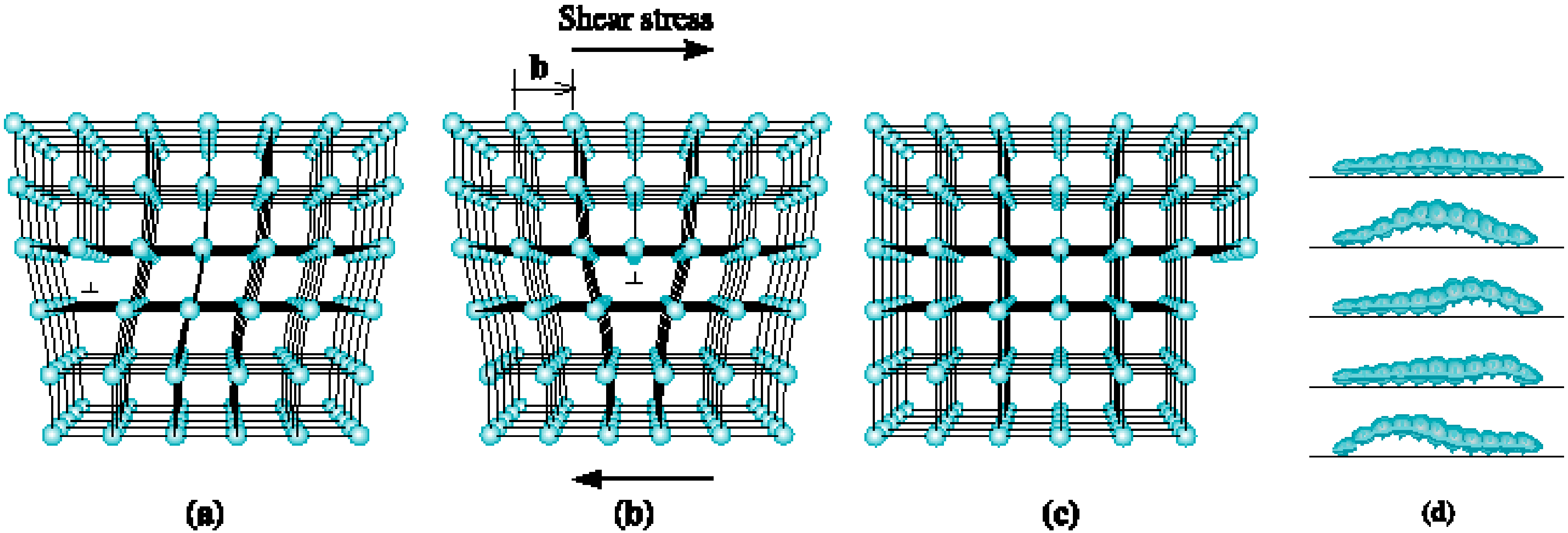
Edge Dislocation



- 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).

- Burgers vector $b \perp$ dislocation line

Motion of Edge Dislocation



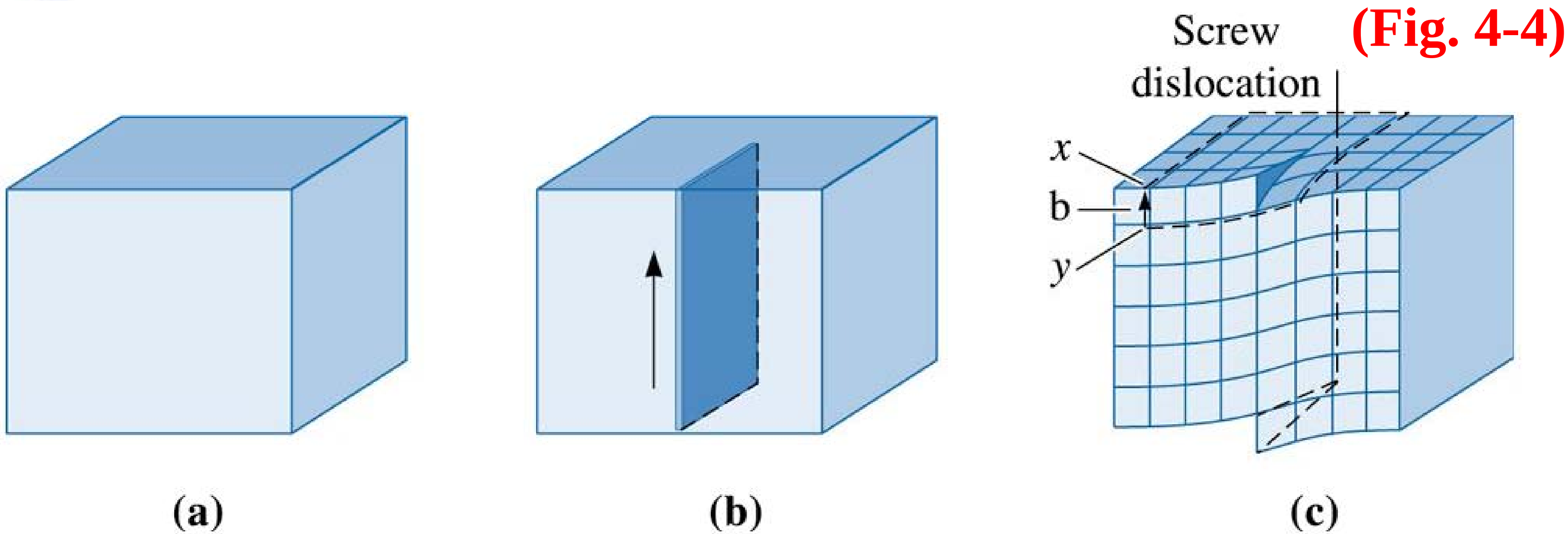
(a) When a shear stress is applied to the dislocation.

(b) The atoms are displaced, causing the dislocation to move one Burgers vector in the slip direction.

(c) Continued movement of the dislocation eventually creates a step, and the crystal is deformed.

(d) Motion of caterpillar is analogous to the motion of a dislocation.

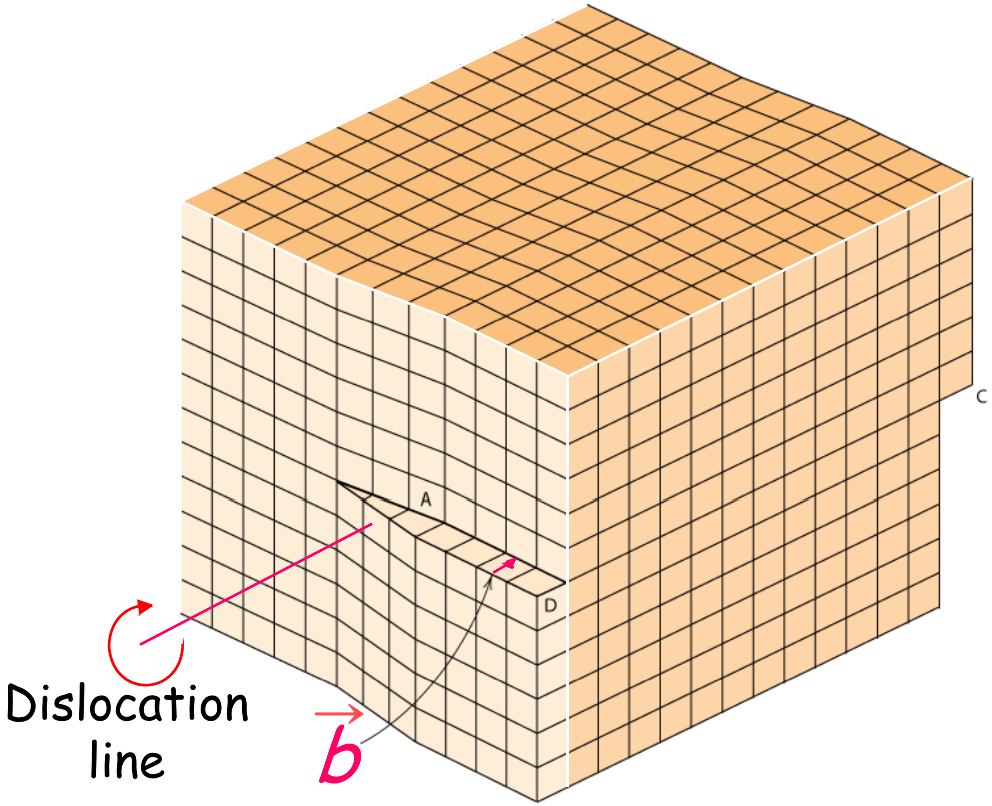
Screw Dislocation

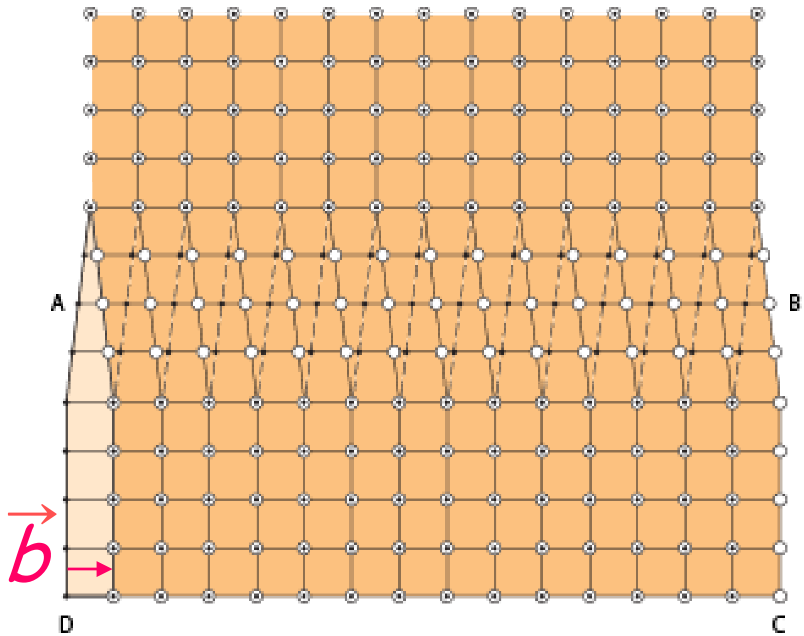


- The perfect crystal (a) is cut and sheared by one atom spacing. The line along which shearing occurs is a screw dislocation.
- A Burgers vector *b* is required to close a loop of equal atom spacing around the screw dislocation → magnitude & direction of the lattice distortion
- Burgers vector *b* // dislocation line

Screw Dislocation

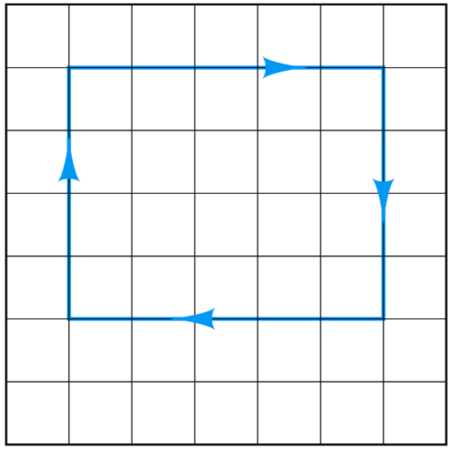
(Fig. 4-4)



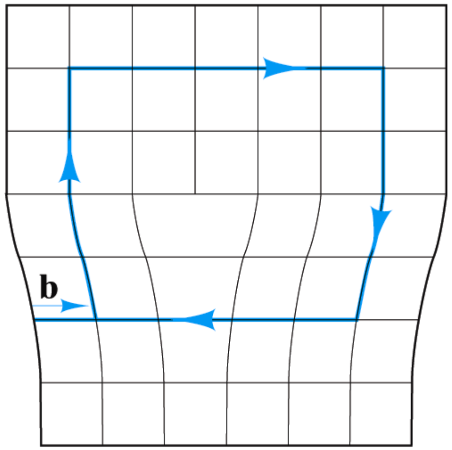


Burger's Vector, *b*

perfect crystal



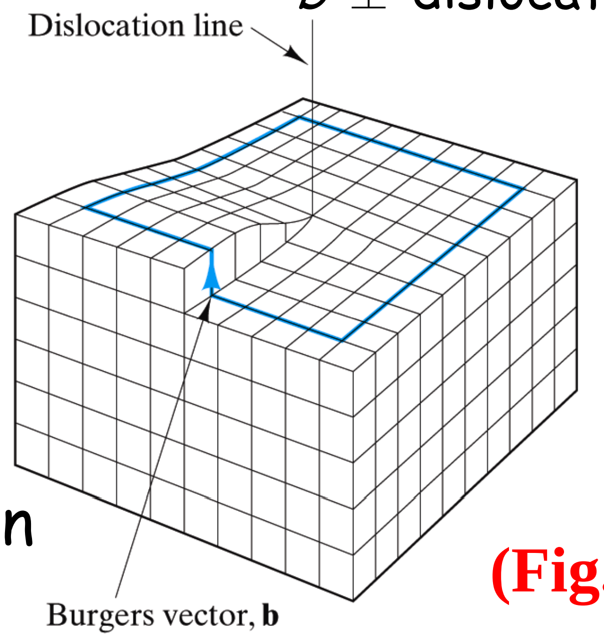
edge dislocation



(Fig. 4-3)

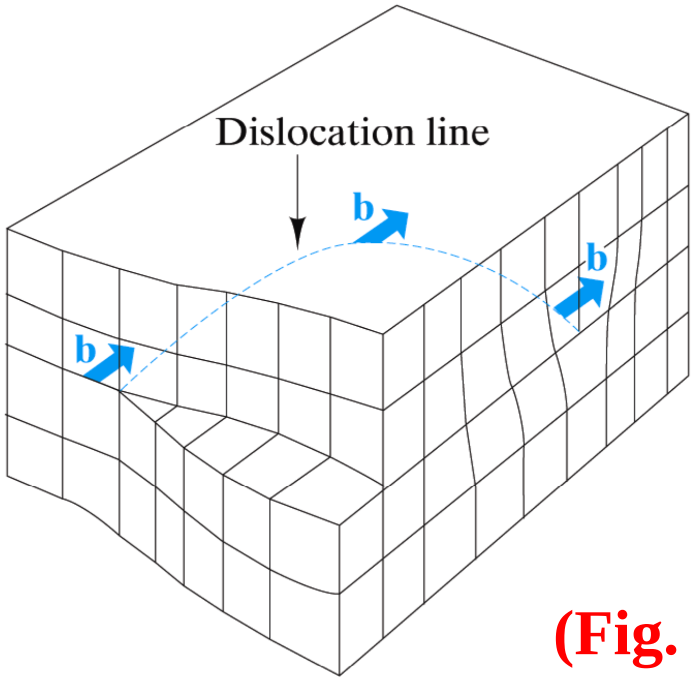
✓ Represents the magnitude of the structural defect

b ⊥ dislocation line



screw dislocation

(Fig. 4-4)



(Fig. 4-5)

mixed dislocation

Linear Defects (Dislocations):

one-dimensional defects around which atoms are misaligned

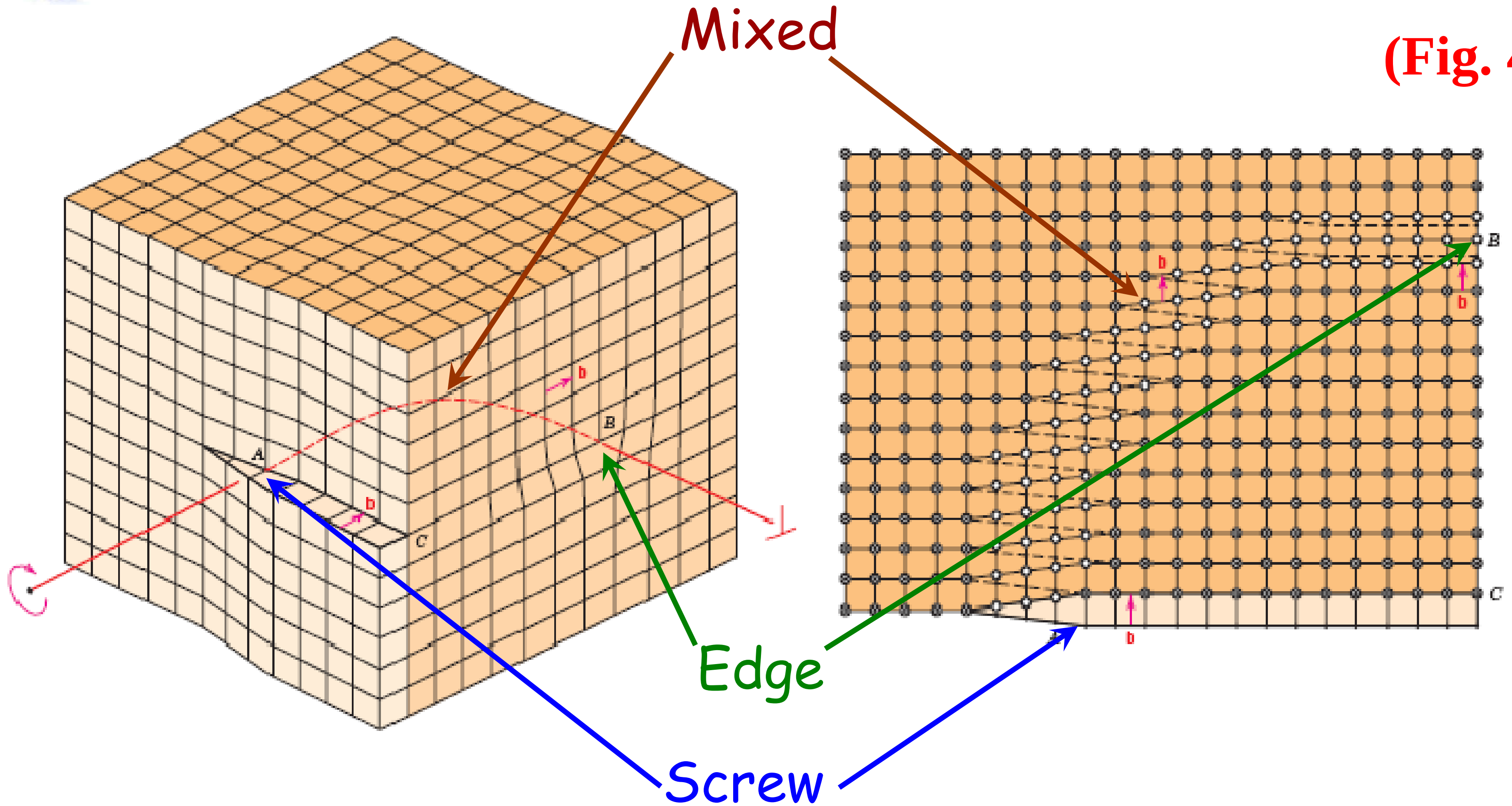
- **Edge dislocation:**
  - ✓ extra half-plane of atoms inserted in a crystal structure
  - ✓ $\vec{b} \perp$ dislocation line

- **Screw dislocation:**
  - ✓ spiral planar ramp resulting from shear deformation
  - ✓ $\vec{b} \parallel$ dislocation line

Burger's vector, $\vec{b}$: measure of lattice distortion

Mixed Dislocation

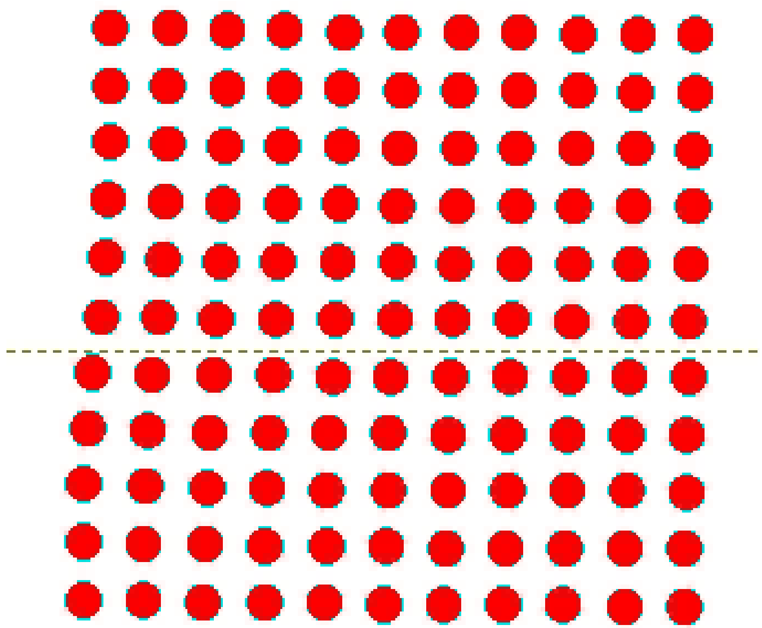
(Fig. 4-5)



The screw dislocation at the front face of the crystal gradually changes to an edge dislocation at the side of the crystal.

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.

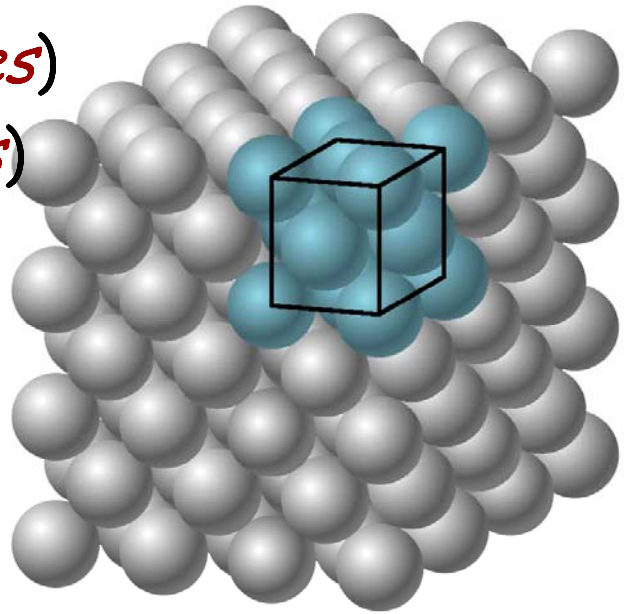


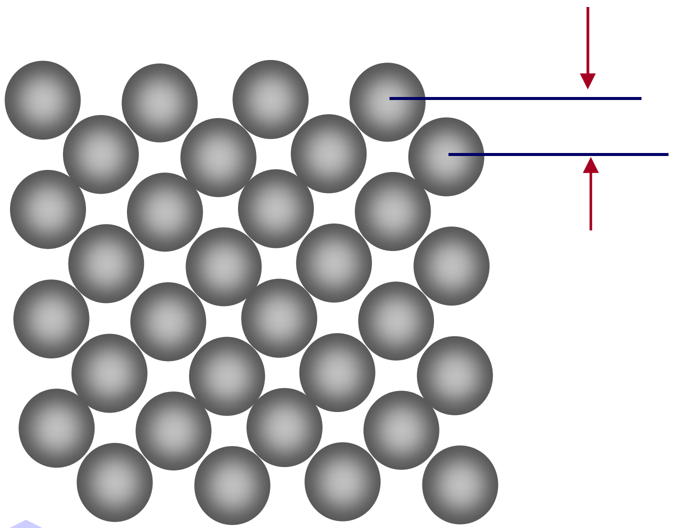
Slip Planes and Slip Directions

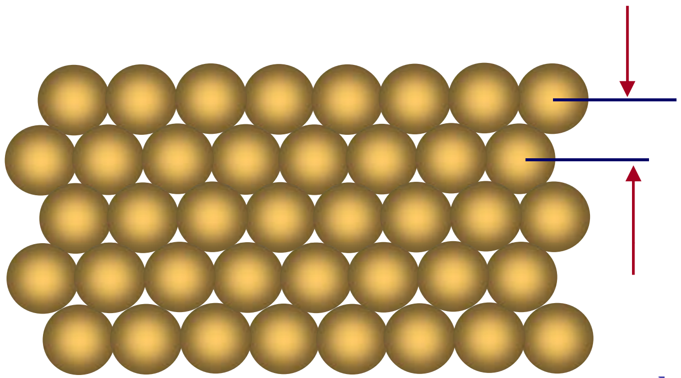
Chapter 7.4

✓ Dislocation mobility is not the same in all crystallographic planes or directions.

✓ There are preferred planes (*slip planes*) and preferred directions (*slip directions*) along which dislocations move with greater ease.







Dislocation

Dislocations are visible in electron micrographs

➢ PLANAR DEFECTS

- ✓ Surface
- ✓ Grain boundary
- ✓ Twin boundary
- ✓ Stacking fault
- ✓ Domain boundary

Surface Defects

(*skip*)

- Surface defects - Imperfections, such as grain boundaries, that form a two-dimensional plane within the crystal
- Hall-Petch equation - The relationship between yield strength and grain size in a metallic material — that is

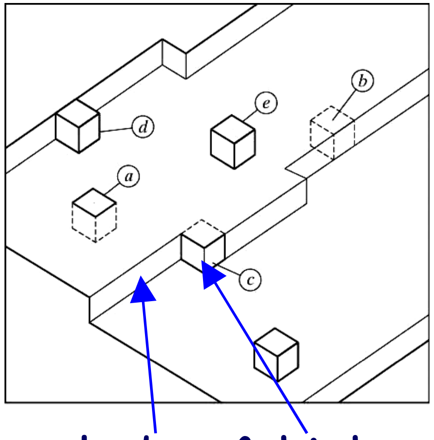
$$\sigma_y = \sigma_0 + K d^{-1/2}$$

- ASTM grain size number (*n*) - A measure of the size of the grains in a crystalline material obtained by counting the number of grains per square inch at a magnification of 100X
- Small angle grain boundary - An array of dislocations causing a small misorientation of the crystal across the surface of the imperfection

Surface Defects

➢ Imperfections, such as grain boundaries, that form a two-dimensional plane within the crystal

Crystal growth from vapor phase around a screw dislocation in SiC.



ledge & kink

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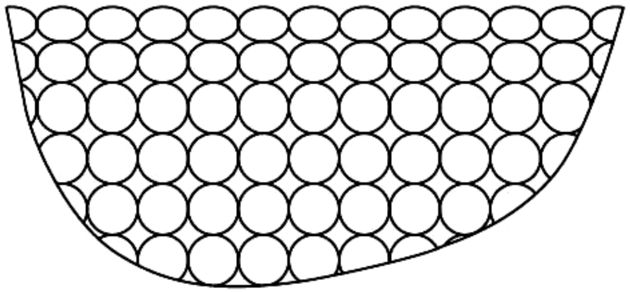


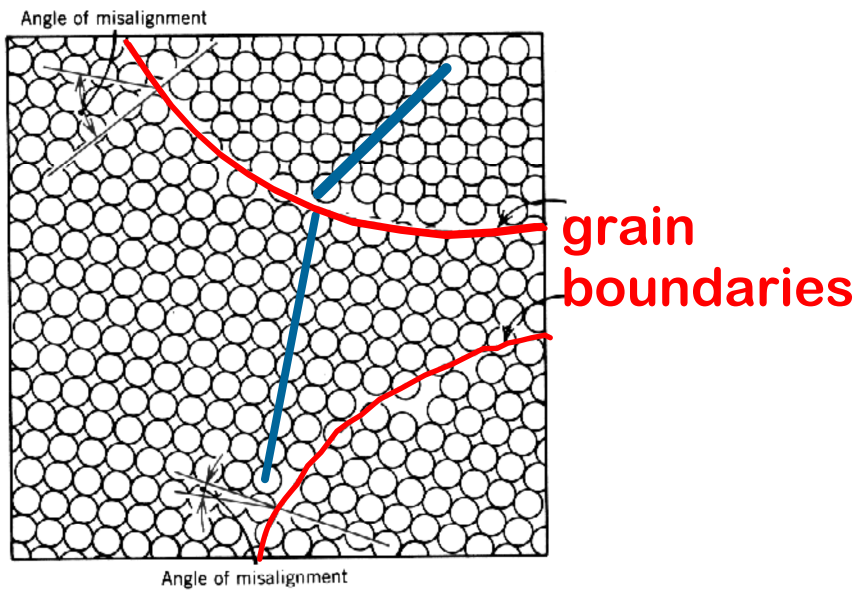
- fewer nearest neighbor in the surface
- higher energy → surface tension or energy

Grain Boundary

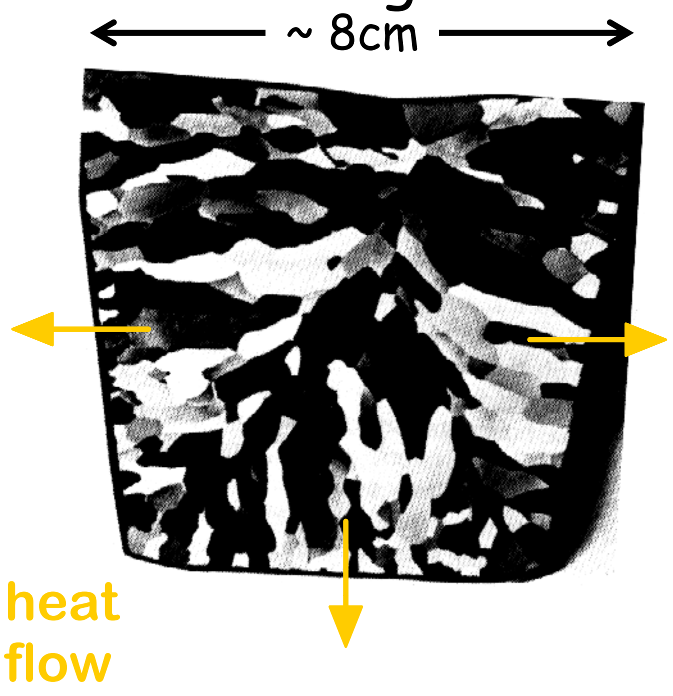
- Boundaries between crystals.
- Produced by the solidification process, for example.
- Change in the crystal orientation across them.
- Impede dislocation motions.

(Fig. 4-7)
(Fig. 4-12)

Schematic

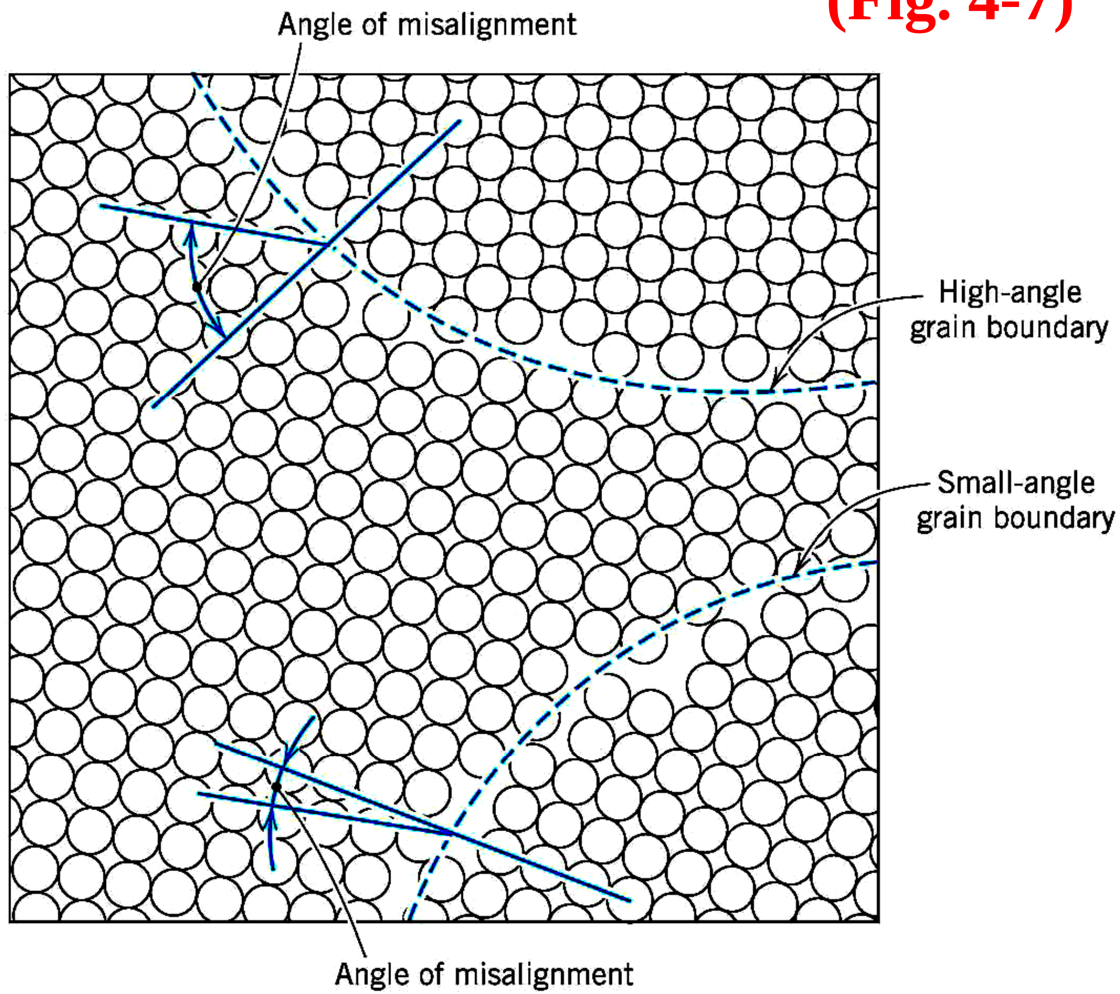


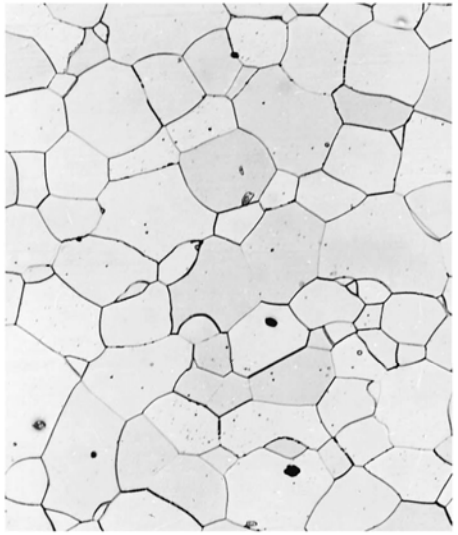
Metal Ingot



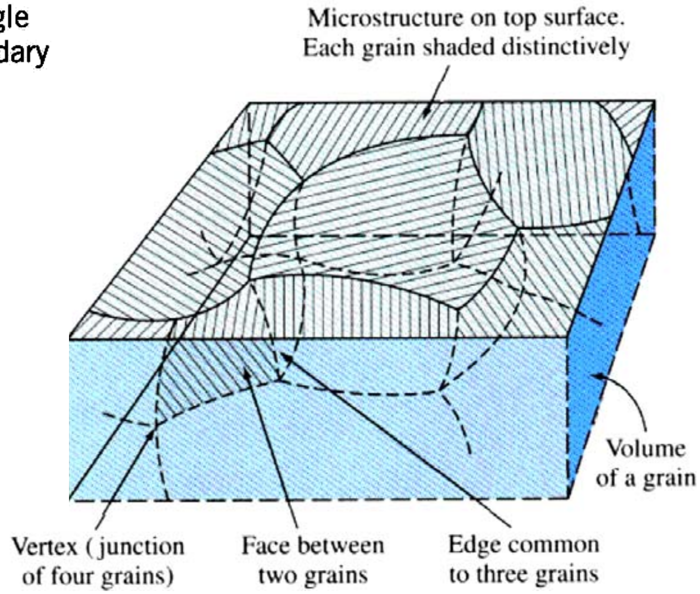
Grain Boundary

(Fig. 4-7)





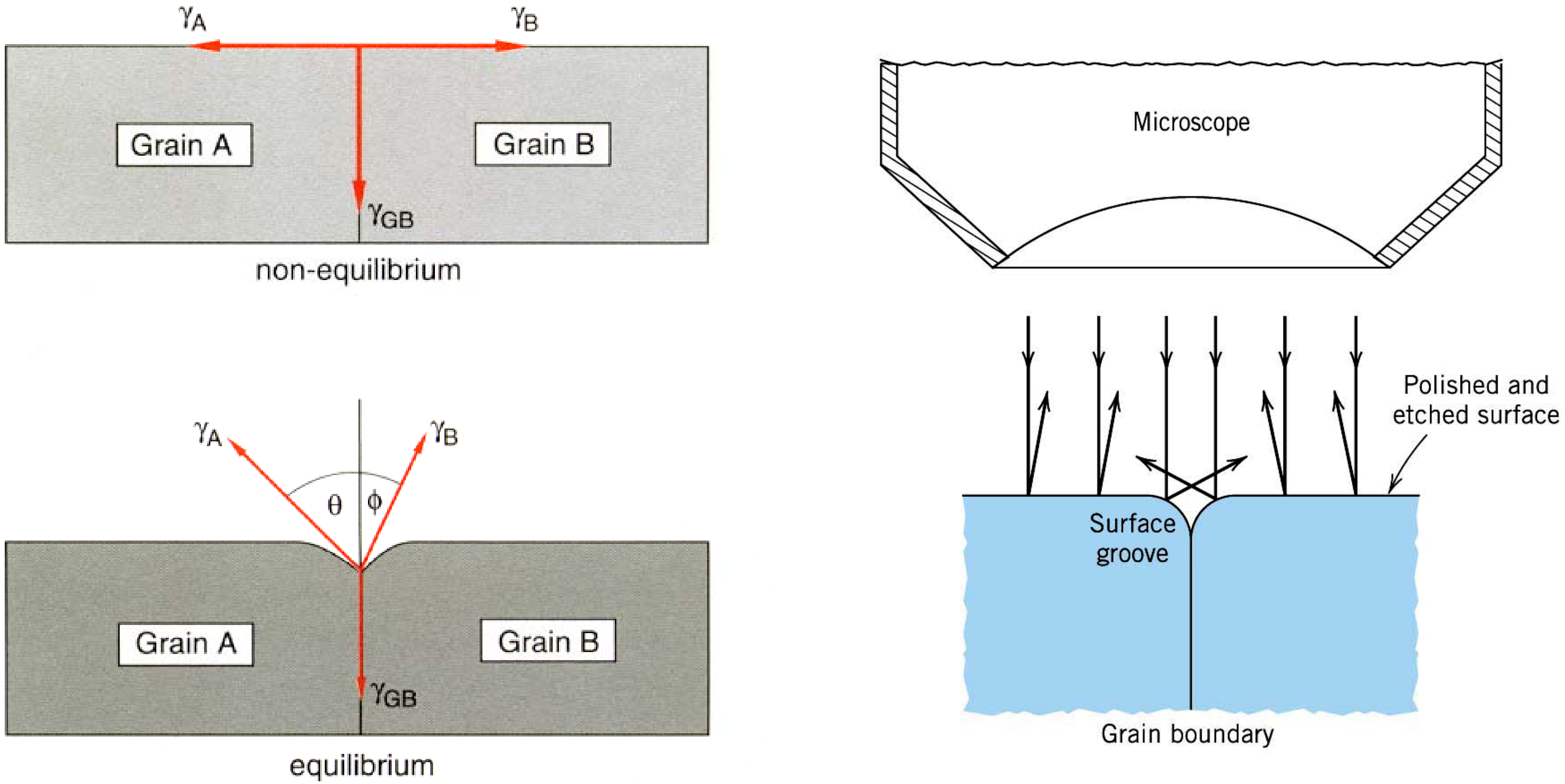
(Fig. 4-14)



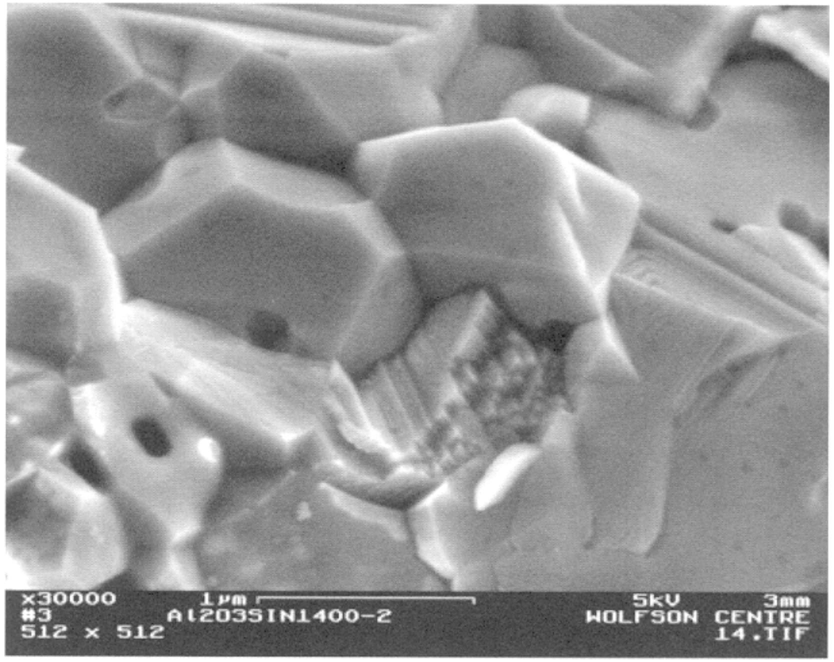
Observation of Grain Boundary

- Chemical etching
- Thermal etching → groove

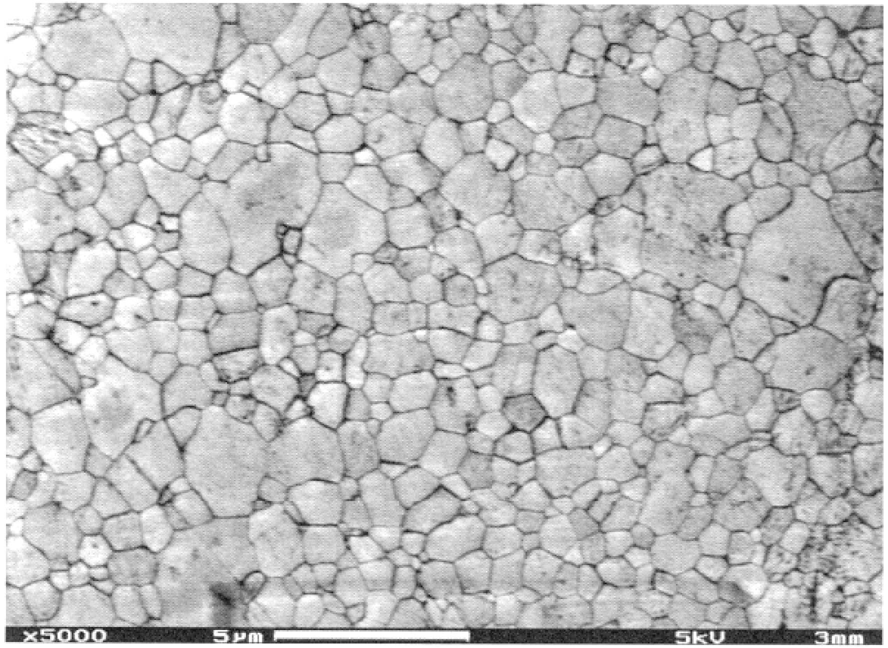
(Fig. 4-13)



Observation of Grain Boundary



fracture surface of alumina



thermally etched alumina

Domain Boundaries

- Domain - a small region of the material in which the direction of electric polarization or magnetization remains the same

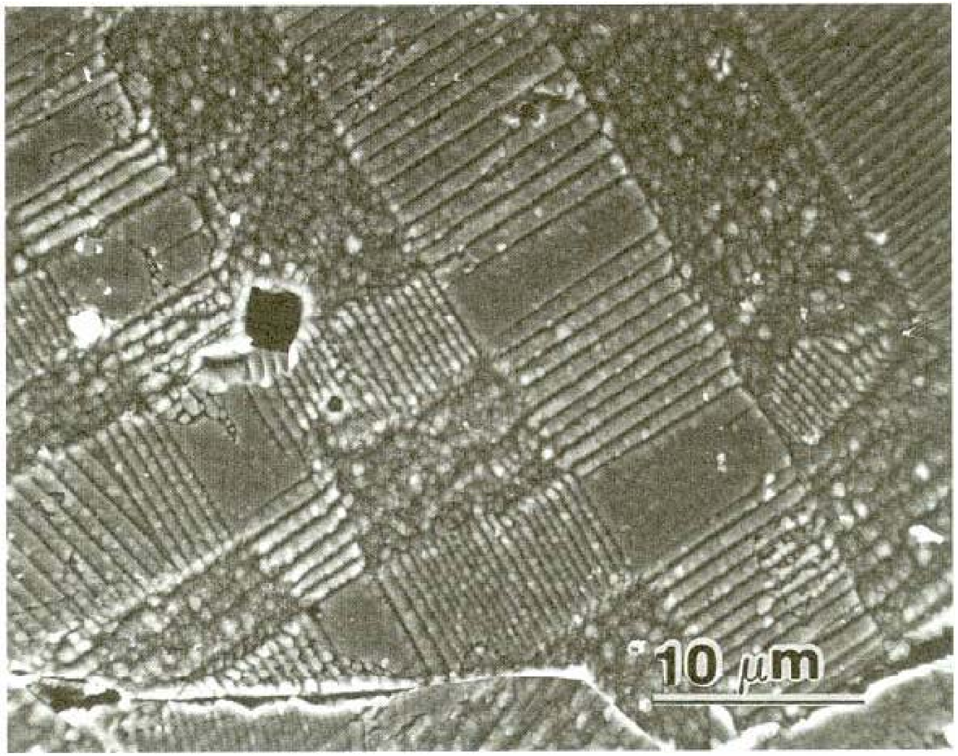


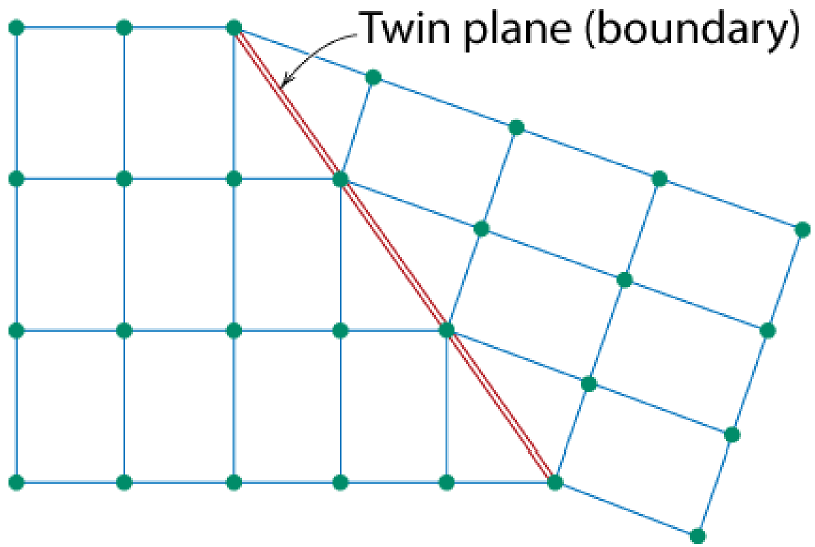
Figure 4-21 Domains in ferroelectric barium titanate. (*Courtesy of Dr. Rodney Roseman, University of Cincinnati.*) Similar domain structures occur in ferromagnetic and ferrimagnetic materials.

Miscellaneous Imperfections

- Twin Boundaries

ABCABCBACBA

Essentially a reflection of atom positions across the twin plane.



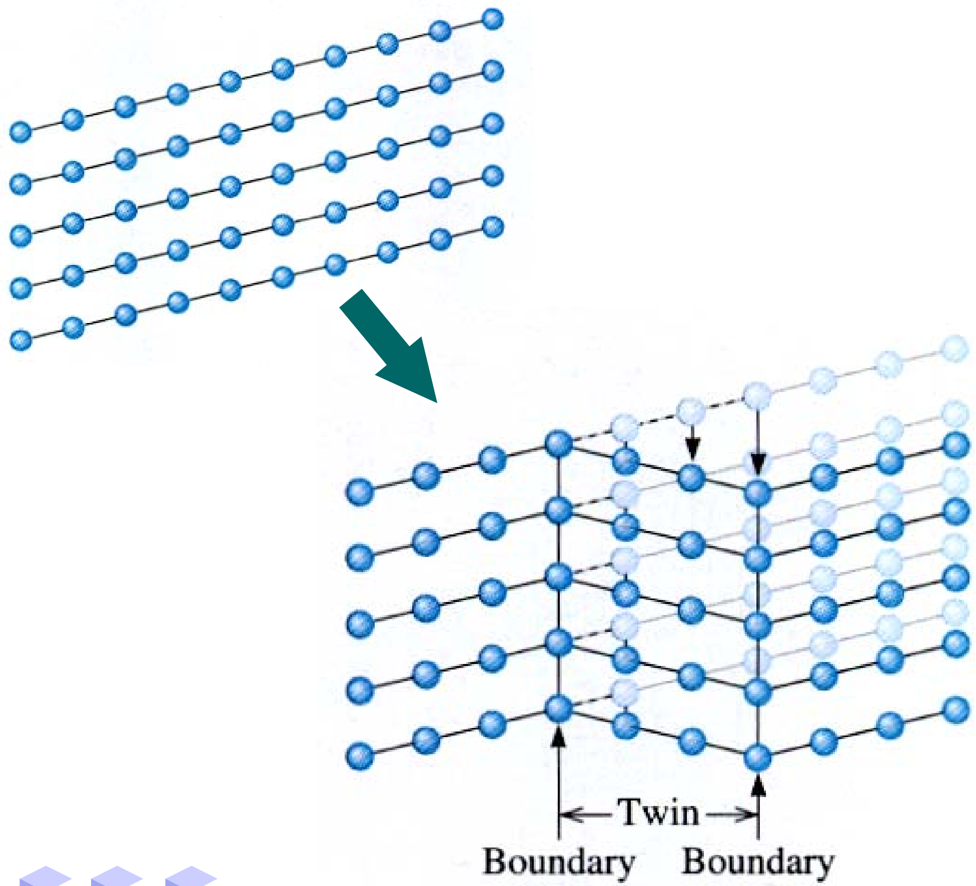
(Fig. 4-9)

- Stacking fault

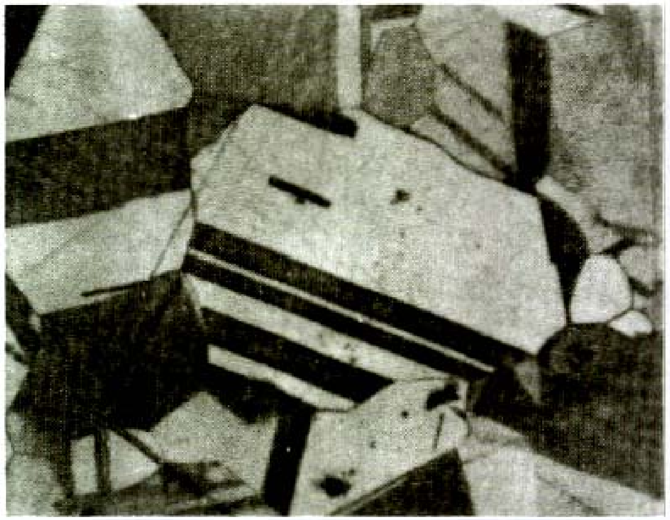
For FCC metals an error in ABCABC packing sequence.
Ex: ABCABABC

Twin Boundary

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

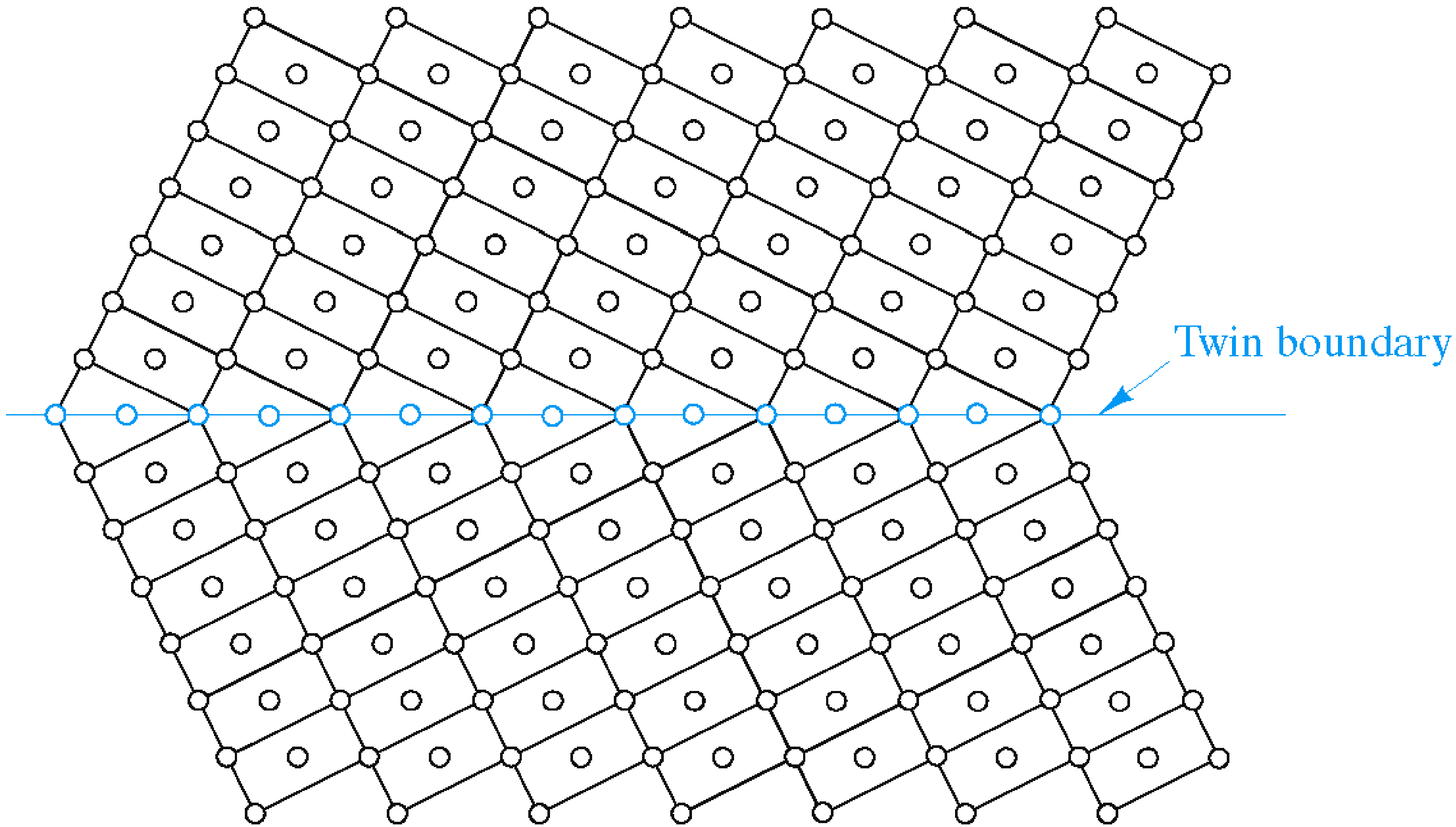


(Fig. 4-13)



Twins within a grain of Brass

Twin Boundary



Contents

Microscopic Examination

- Crystallites (grains) and grain boundaries vary considerably in size. Can be quite large.

  ex: Large single crystal of quartz, diamond, or Si

  ex: Aluminum light post or garbage can - see the individual grains

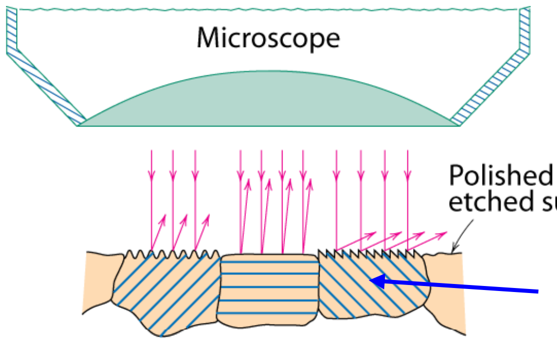
- Crystallites (grains) can be quite small (μm or less) – need to observe with a microscope.

Optical Microscopy

✓ Useful up to 2000X magnification.

✓ Polishing removes surface features (e.g., scratches)

✓ Etching changes reflectance, depending on crystal orientation.



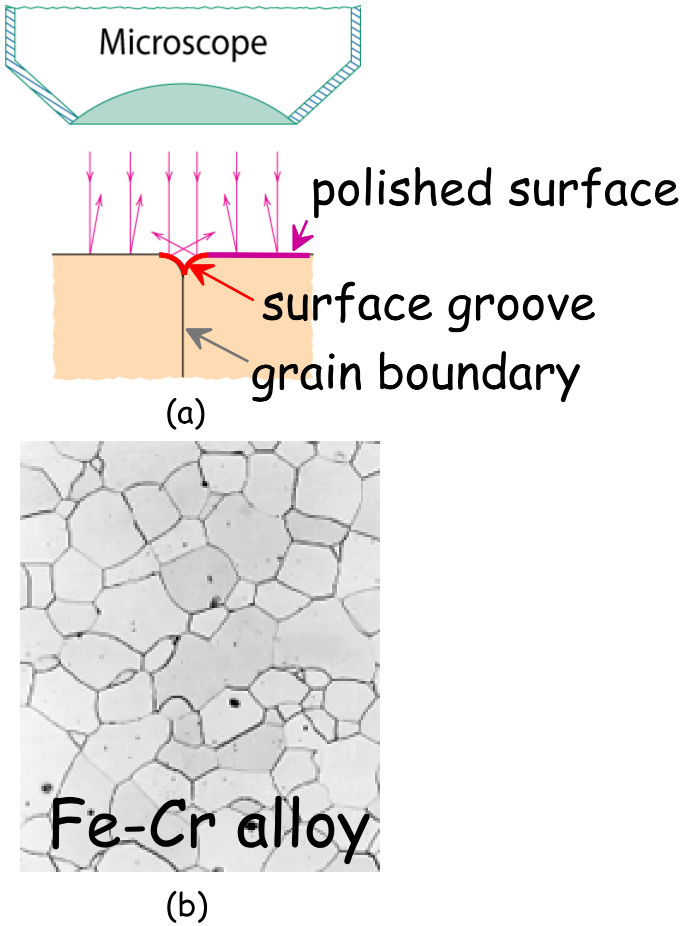
(Fig. 4-13)

Micrograph of brass (Cu-Zn alloy)

Optical Microscopy

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

(Fig. 4-14)



SUMMARY

- Point, Line, and Area defects arise in solids.
- The number and type of defects can be varied and controlled. (*Temperature* controls the vacancy concentrations.)
- Defects affect material properties.

  (Controlling the crystal slip or electronic conductivity.)
- Defects may be desirable or undesirable.

  (Dislocations may be good for the epitaxy of semiconductors. Point defects in diamond may be good for a tool, and bad for wedding).

- Problems from Chap. 4 http://bp.snu.ac.kr

  √ Prob. 4-1 Prob. 4-2 Prob. 4-3 Prob. 4-8 Prob. 4-10

  √ Prob. 4-23 Prob. 4-24 Prob. 4-26 Prob. 4-29 Prob. 4-31