# CHAPTER 4:
# IMPERFECTIONS IN SOLIDS

## ISSUES TO ADDRESS...

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

# Types of imperfections

- Vacancies
- Interstitial atoms
- Substitutional atoms

Point defects

- Dislocations

Line defects

- Grain Boundaries

Area defects

- Pores, voids

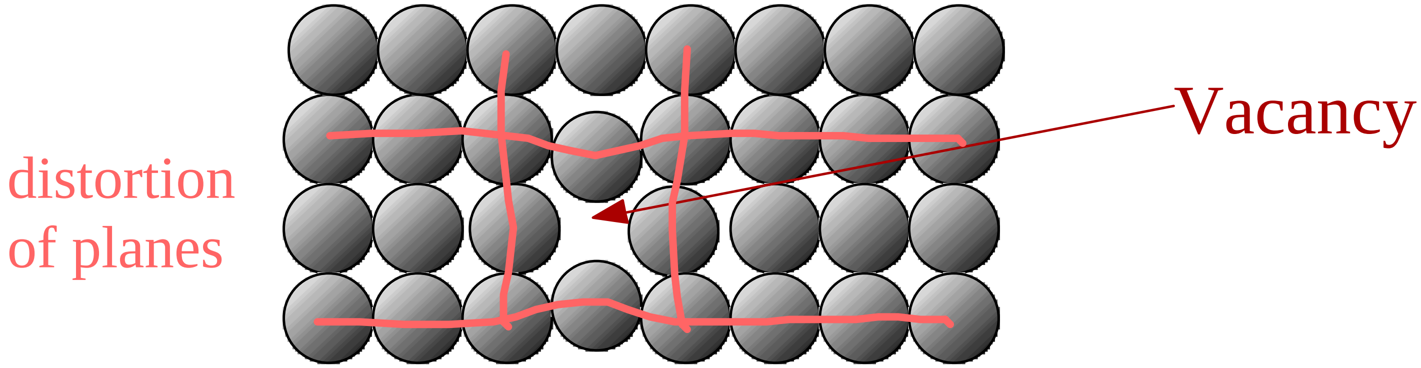
Volume defects

- Atomic vibrations

# Point defects

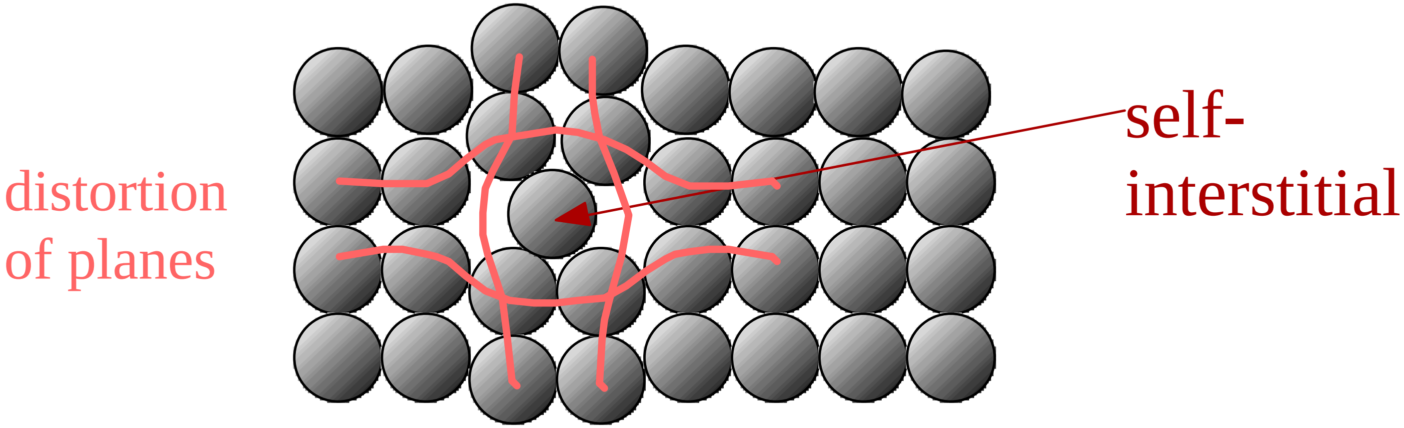
- Vacancies:

  -vacant atomic sites in a structure.




- Self-Interstitials:

  -"extra" atoms positioned between atomic sites.



# Equilibrium concentration: point defects

- Equilibrium concentration of varies with temperature!

No. of defects

Activation energy

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

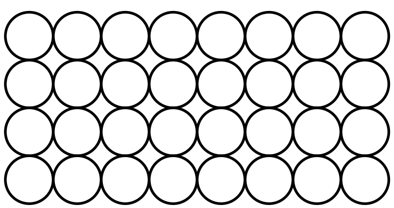
No. of potential defect sites.

Temperature

Boltzmann's constant

$(1.38 \times 10^{-23}$ J/atom K)

$(8.62 \times 10^{-5}$ eV/at om K)



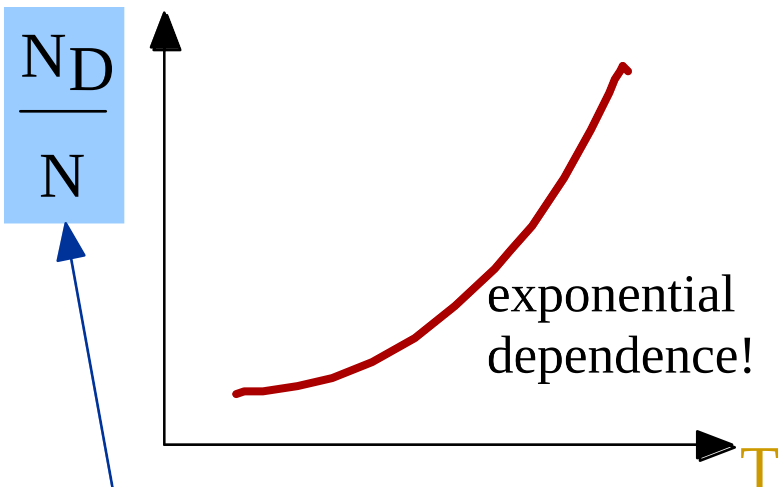
Each lattice site is a potential vacancy site

# Measuring activation energy

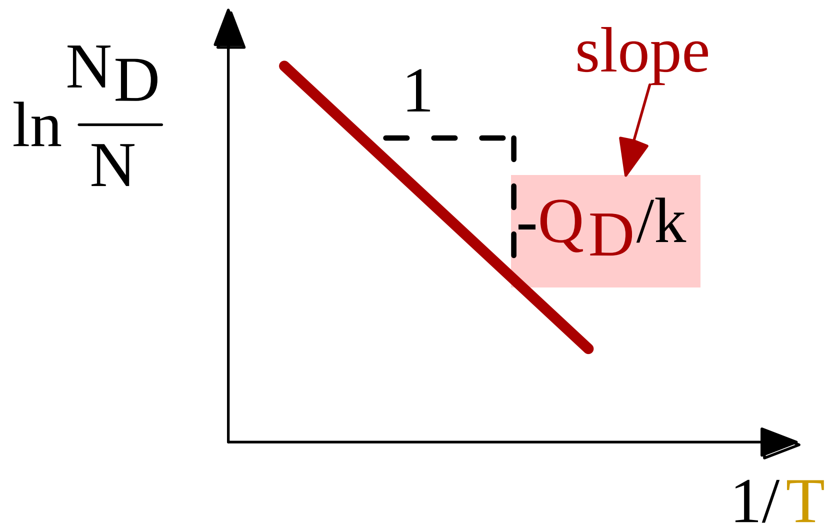
- We can get Q from an experiment.

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

- Measure this...
- Replot it ...




defect concentration



# Estimating vacancy concentration

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

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

$$Q_V = 0.9 \text{eV/atom} \qquad N_A = 6.02 \times 10^{23} \text{ atoms/mole}$$

$$\frac{N_D}{N} = \exp\left(\frac{-Q_D}{kT}\right) = 2.7 \cdot 10^{-4}$$

0.9eV/atom

1273K

$8.62 \times 10^{-5}$ eV/atom-K

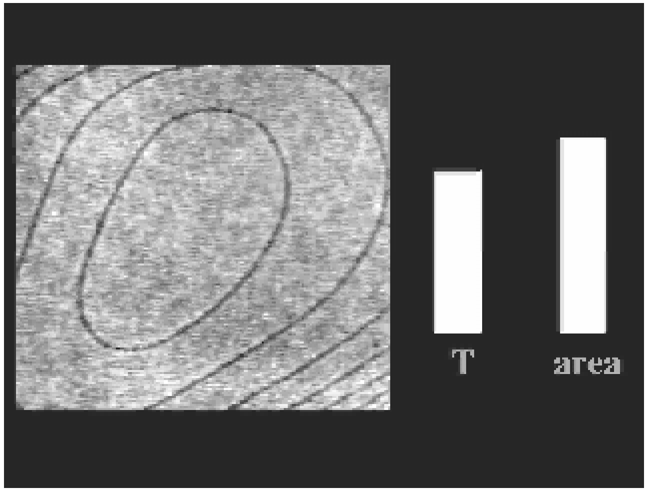
For 1m$^3$, $N = \rho \times \dfrac{N_A}{A_{Cu}} \times 1\text{m}^3 = 8.0 \times 10^{28}$ sites

- Answer:

$$N_D = 2.7 \cdot 10^{-4} \cdot 8.0 \times 10^{28} \text{ sites} = 2.2 \times 10^{25} \text{ vacancies}$$

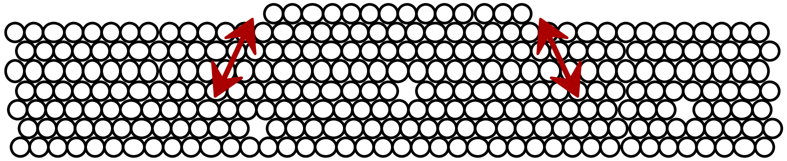
# Observing equilibrium vacancy conc.

- Low energy electron microscope view of a (110) surface of NiAl.
- Increasing T causes surface island of atoms to grow.
- Why? The equil. vacancy conc. increases via atom motion from the crystal to the surface, where they join the island.




Reprinted with permission from Nature (K.F. McCarty, J.A. Nobel, and N.C. Bartelt, "Vacancies in Solids and the Stability of Surface Morphology", Nature, Vol. 412, pp. 622-625 (2001). Image is 5.75 μm by 5.75 μm.) Copyright (2001) Macmillan Publishers, Ltd.

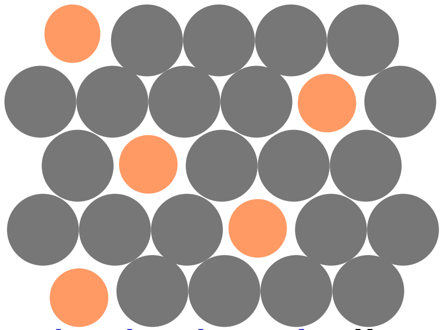
Island grows/shrinks to maintain equil. vacancy conc. in the bulk.



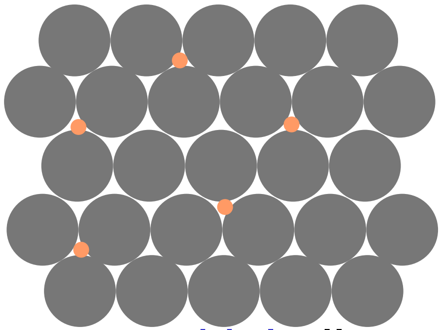
# Point defects in alloys

Two outcomes if impurity (B) is added to host (A):

- Solid solution of B in A (i.e., random dist. of point defects)



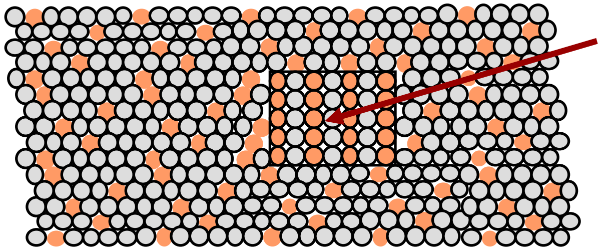
OR



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

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

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



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

# Criteria for substitutional dissolution

Example of Cu-Ni alloys

- Atomic size
  - Atomic radii are within 15% (Cu:1.28A; Ni:1.25A)
- Crystal structure
  - They have similar crystal structure (Cu:FCC; Ni:FCC)
- Electronegativity
  - Intermetallic compound will form if they are vastly differents (Cu:1.9; Ni:1.8)
- Valences
  - Metals dissolve metal of higher valence (Cu:+1; Ni:+2)

# Interstitial dissolution

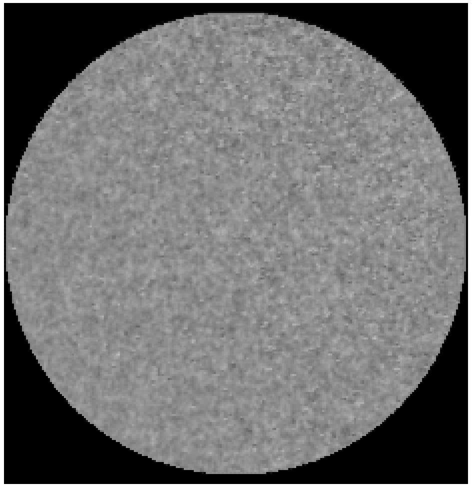
Close packed structures (FCC, HCP) do not have much room to accommodate interstitial atoms (tetrahedral, octahedral sites). Neither does BCC.

Interstitial atoms must be very small to fit in space without straining the crystal lattice

Steel – C-Fe alloy: C (0.071A) occupies small interstitial space in BCC or FCC iron (1.24A). Solubility is quickly exceeded (0.02 wt% in BCC. 2 wt% in FCC).

# alloying a surface

- Low energy electron microscope view of a (111) surface of Cu.
- Sn islands move along the surface and "alloy" the Cu with Sn atoms, to make "bronze".
- The islands continually move into "unalloyed" regions and leave tiny bronze particles in their wake.
- Eventually, the islands disappear.



Reprinted with permission from: A.K. Schmid, N.C. Bartelt, and R.Q. Hwang, "Alloying at Surfaces by the Migration of Reactive Two-Dimensional Islands", Science, Vol. 290, No. 5496, pp. 1561-64 (2000). Field of view is 1.5 $\mu$m and the temperature is 290K.

# Composition

Definition: Amount of impurity (B) and host (A) in the system.

Two descriptions:

- Weight %

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

- Atom %

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

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

$$C_B = \frac{C'_B A_B}{C'_A A_A + C'_B A_B} \times 100$$

$$C'_B = \frac{C_B / A_B}{C_A / A_A + C_B / A_B}$$

- Basis for conversion:

mass of B = moles of B x $A_B$

mass of A = moles of A x $A_A$

atomic weight of B

atomic weight of A

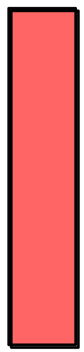
# Line defects

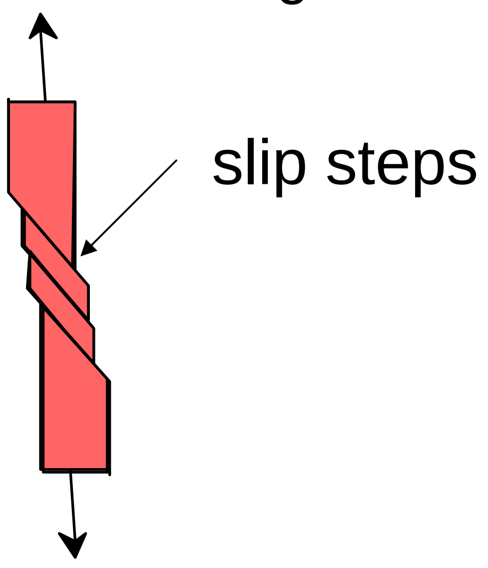
Dislocations:

- are line defects,
- cause slip between crystal plane when they move,
- produce permanent (plastic) deformation.

Schematic of a Zinc (HCP):

- before deformation
- after tensile elongation



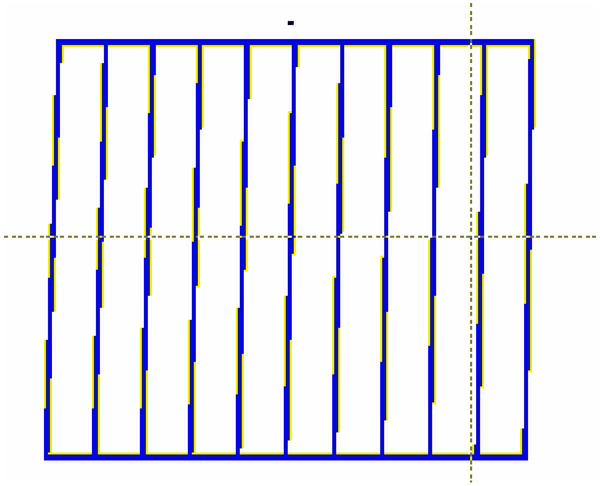


# Incremental slip

- Dislocations slip planes *incrementally*...
- The dislocation line (the moving red dot)...

  ...separates slipped material on the left

  from unslipped material on the right.

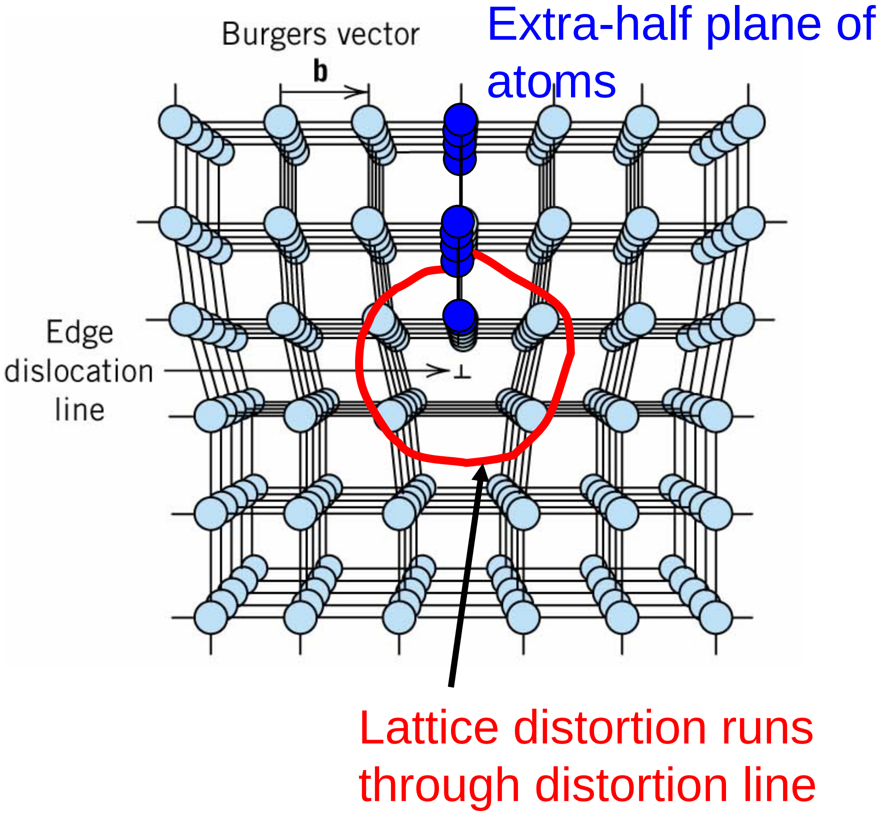


Simulation of dislocation motion from left to right as a crystal is sheared.

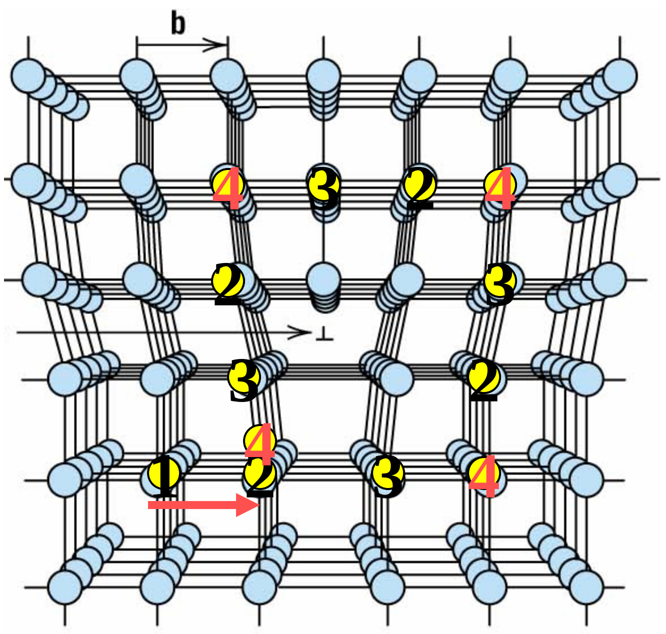
(Courtesy P.M. Anderson)

# Edge dislocation

Burger’s vector - Magnitude and direction of lattice distortion. (Unit of atomic displacement  in the direction of slip.)



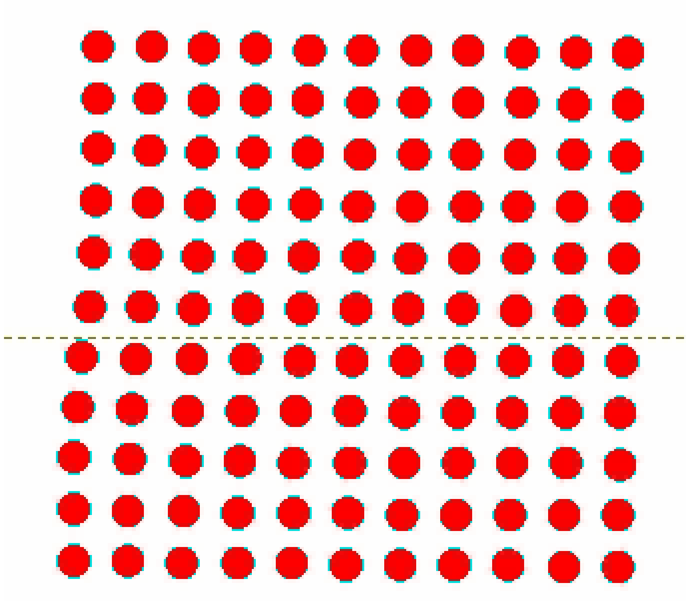

Finding the Burger’s vector




b ⊥ 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.

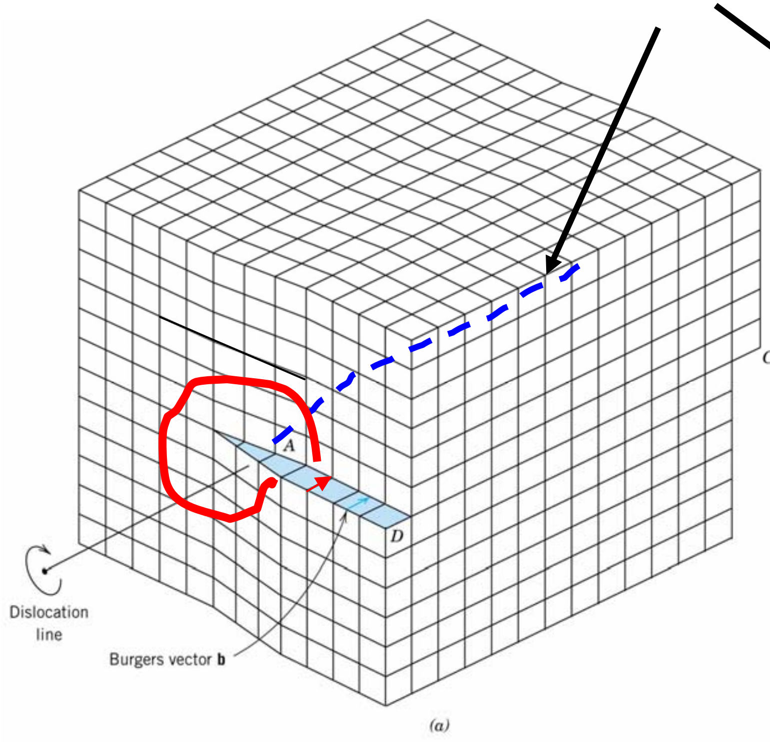


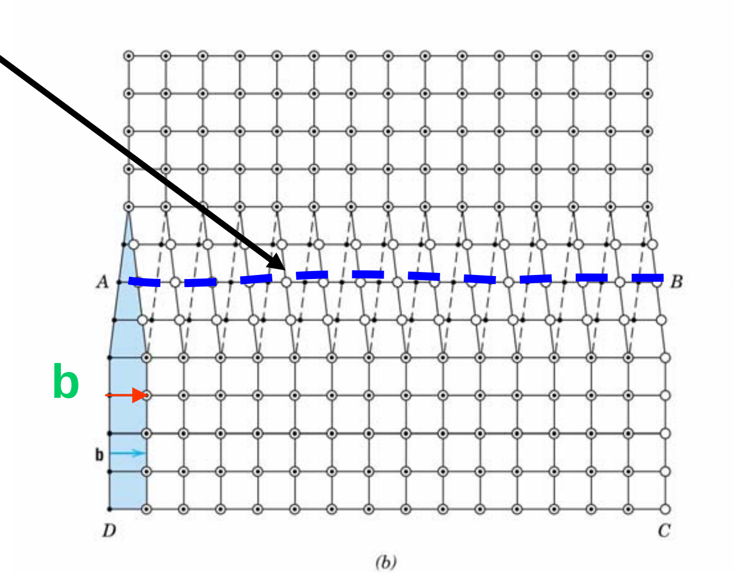
Atomic view of edge dislocation motion from left to right as a crystal is sheared.

(Courtesy P.M. Anderson)

# Screw dislocations

Screw dislocation line

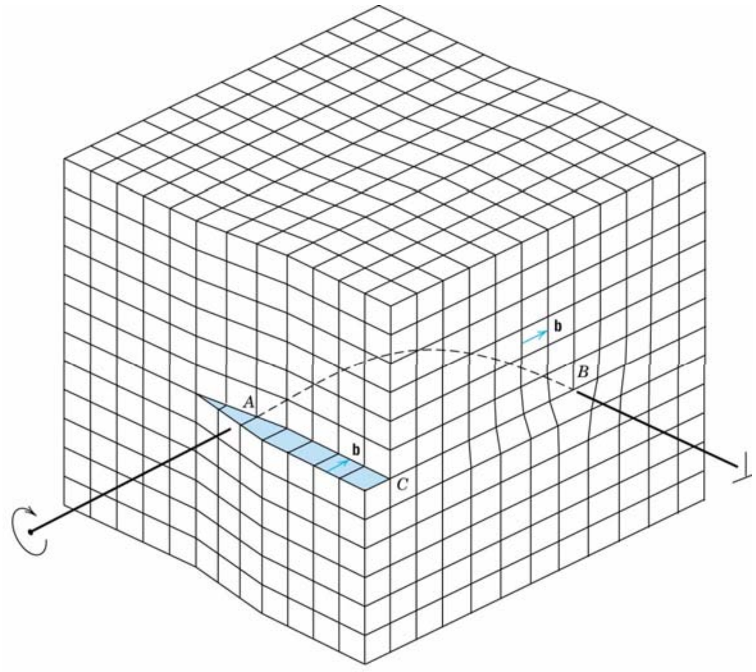


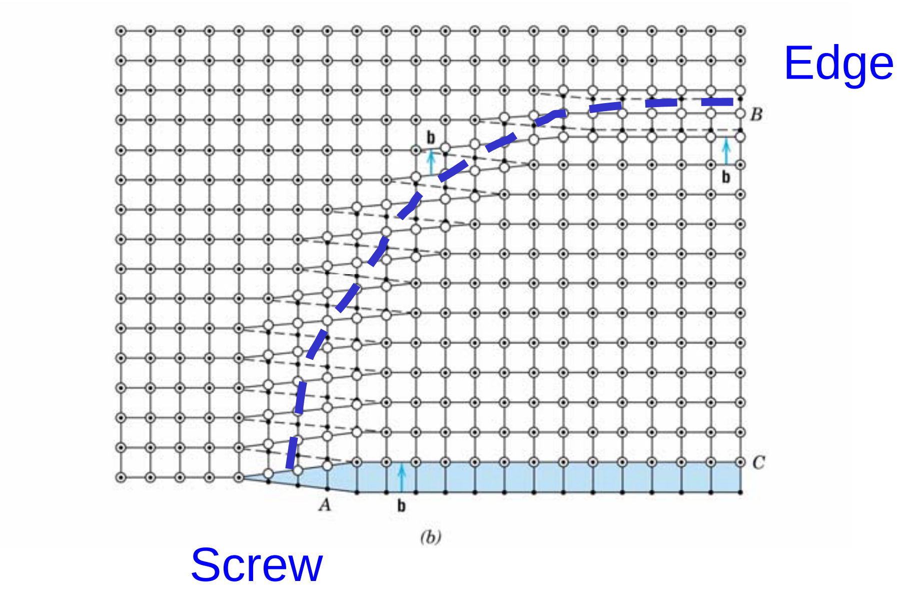

b // dislocation line

Lattice distortion runs through dislocation line

# Mixed dislocation



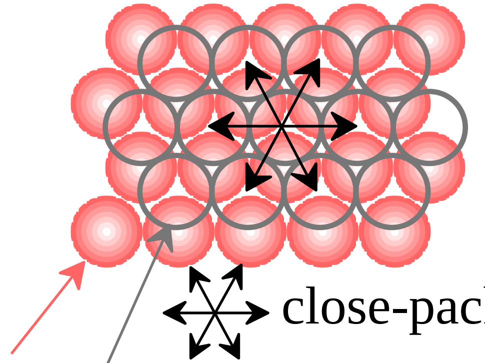
(a)



(b)

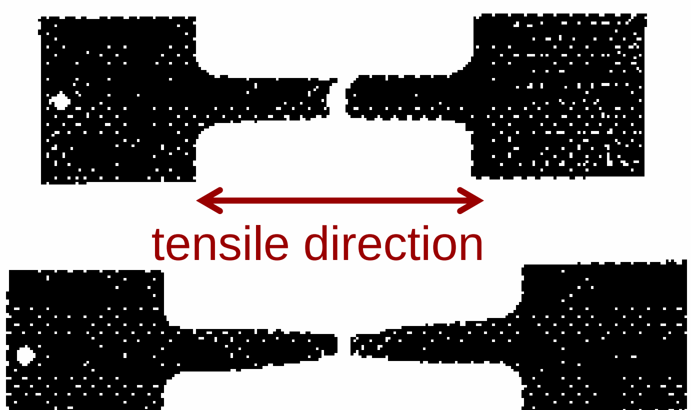
# Dislocations & crystal structure

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




- Comparison among crystal structures:
  FCC: many close-packed planes/directions 4/3;
  HCP: only one plane, 3 directions;
  BCC: none – slip is possible on other planes but more difficult

- Results of tensile testing.

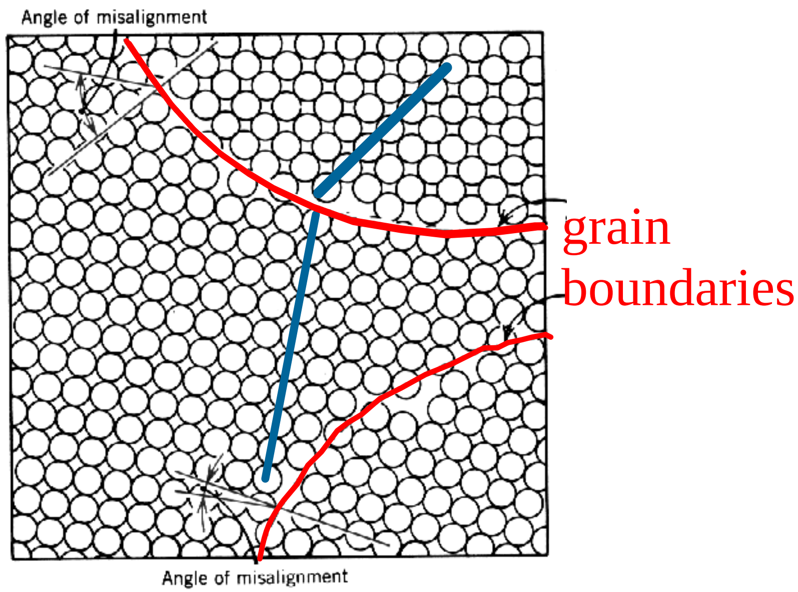


# Area defects: grain boundaries

Grain boundaries:

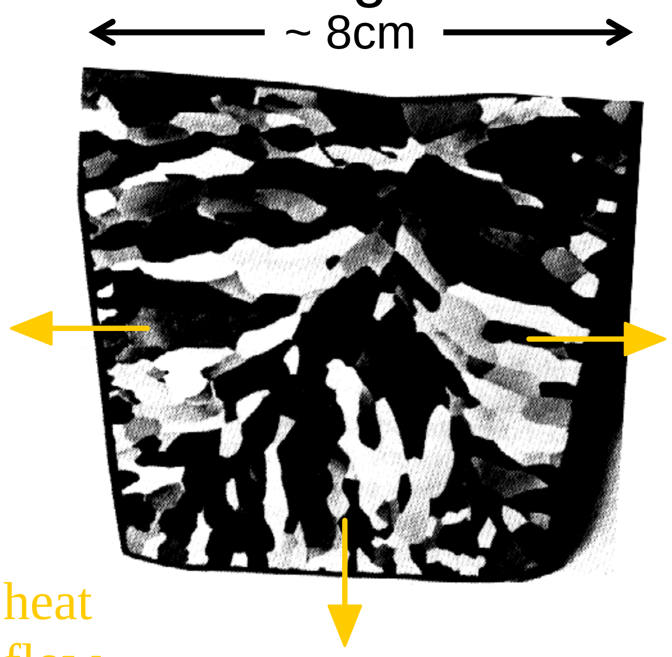
- are boundaries between crystals.
- are produced by the solidification process, for example.
- have a change in crystal orientation across them.
- impede dislocation motion.

Schematic




Adapted from Fig. 4.7, *Callister 6e.*

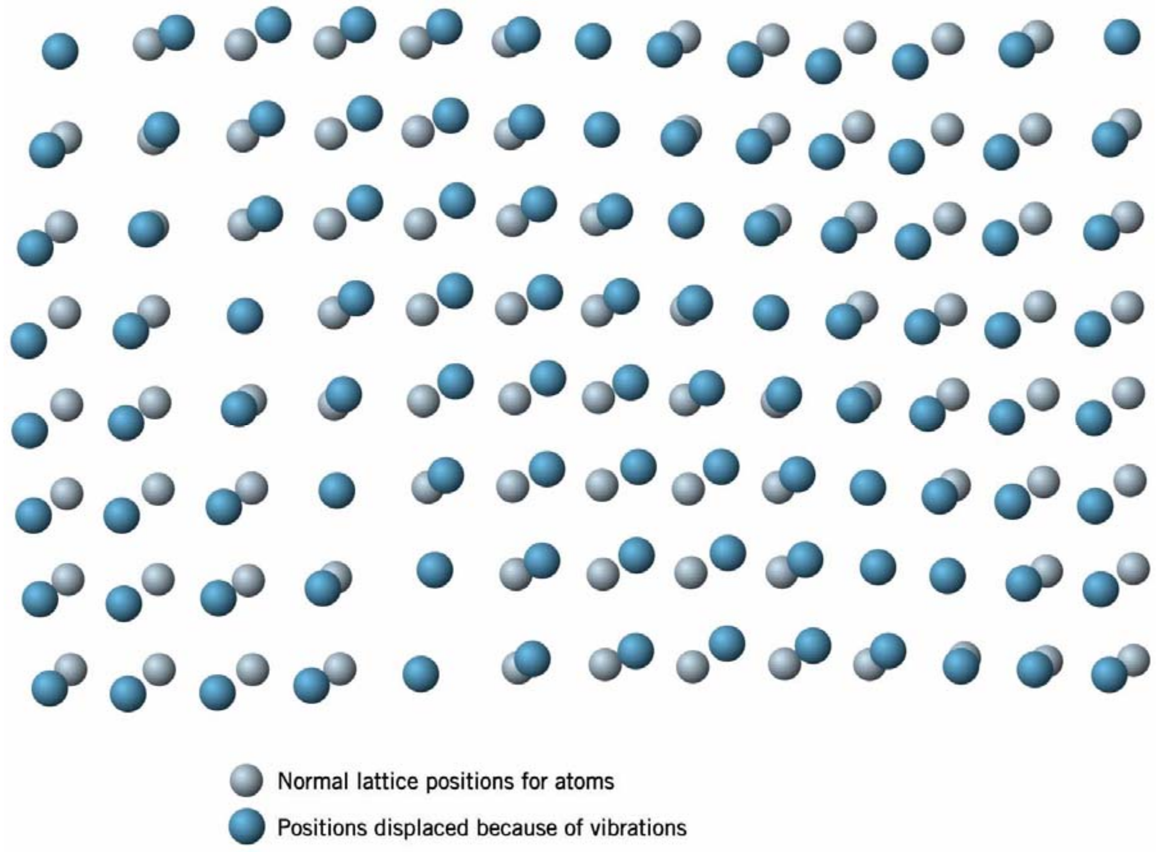
Metal Ingot




Adapted from Fig. 4.10, *Callister 6e.* (Fig. 4.10 is from *Metals Handbook*, Vol. 9, 9th edition, *Metallography and Microstructures*, Am. Society for Metals, Metals Park, OH, 1985.)

# Lattice vibration

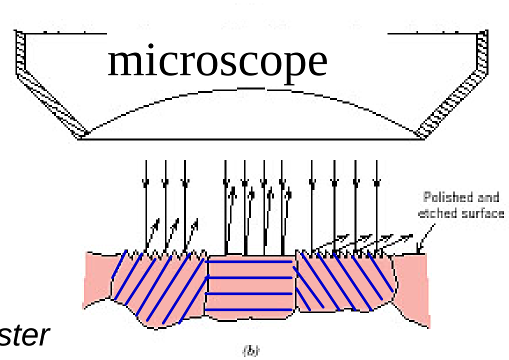
- Freeze-time model of atoms in a crystal – Lattice vibration may be thought of as a defect since atoms are no longer at their perfect lattice sites




Lattice vibration is a mode of heat transfer through a crystal

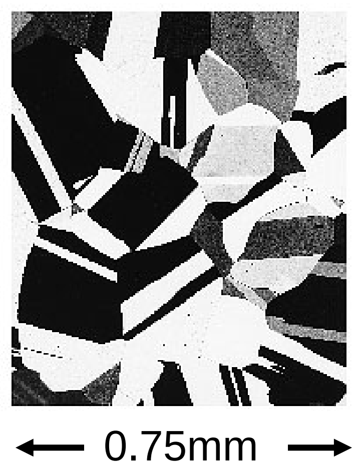
# Optical microscopy (1)

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




close-packed planes

Adapted from Fig. 4.11(b) and (c), *Callister 6e.* (Fig. 4.11(c) is courtesy of J.E. Burke, General Electric Co.




micrograph of Brass (Cu and Zn)

# Optical microscopy (2)

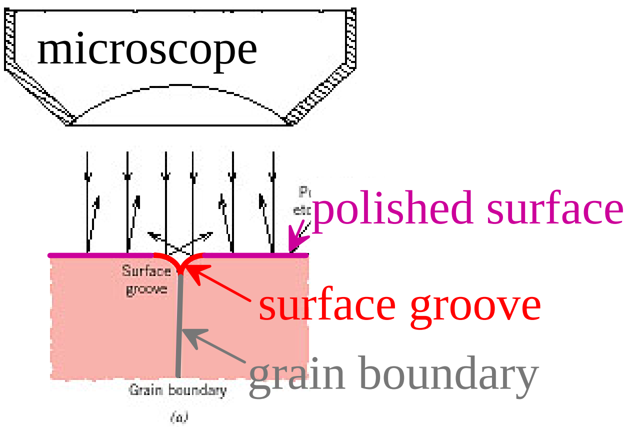
Grain boundaries...

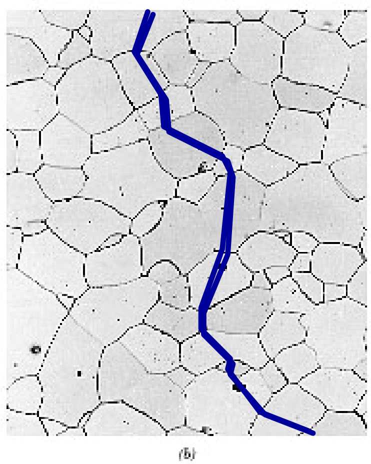
- are imperfections,
- are more susceptible to etching,
- may be revealed as dark lines,
- change direction in a polycrystal.

ASTM grain size number

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

no. grains/in $^2$ at 100x magnification




Adapted from Fig. 4.12(a) and (b), *Callister 6e.* (Fig. 4.12(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].)

# SUMMARY

- Point, Line, and Area, volume defects arise in solids.

- The number and type of defects can be varied and controlled (e.g., T controls vacancy conc.)

- 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.)

- Vibration of all atoms in a crystal about their equilibrium positions may be thought as a defect (melting thought as rupture of large number of atomic bonds)

# ANNOUNCEMENTS

Reading: 4:1-10

Core Problems: 4:3, 4, 14, 26

Self-help Problems:

- Review solved problems in textbook
- Review “Learning Objectives” in textbook