# CHP 4: IMPERFECTIONS IN SOLIDS

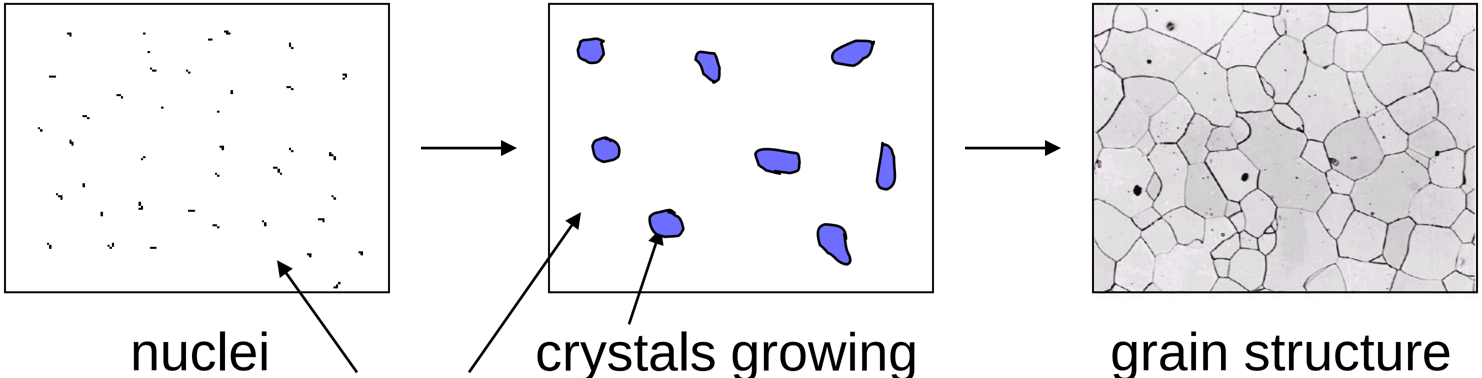
## ISSUES TO ADDRESS...

- What are the solidification mechanisms?
- 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?

# Imperfections in Solids

- Solidification- result of casting of molten material
  - 2 steps
    - Nuclei form
    - Nuclei grow to form crystals – grain structure

- Start with a molten material – all liquid



nuclei

liquid

crystals growing

grain structure

- Crystals grow until they meet each other

# Types of Imperfections

- Vacancy atoms
- Interstitial atoms
- Substitutional atoms

Point defects

- Dislocations

Line defects

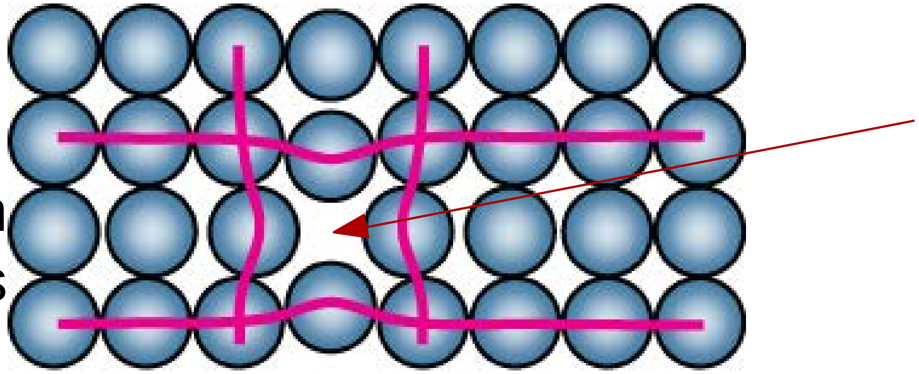
- Grain Boundaries

Area defects

# Point Defects

- **Vacancies**:

  -vacant atomic sites in a structure.

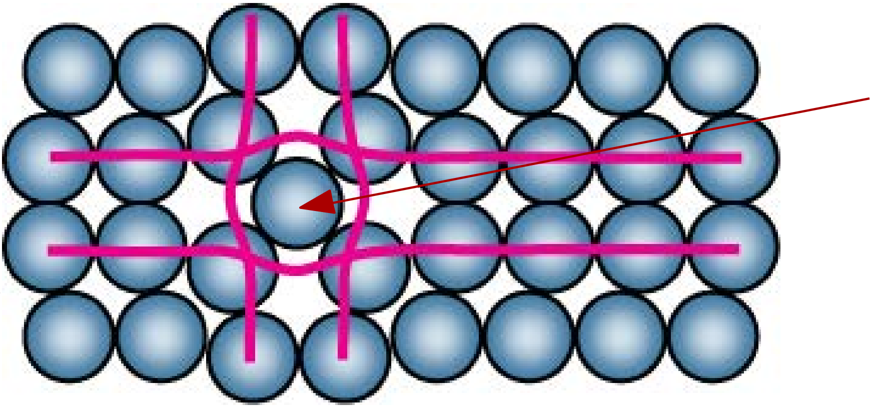


distortion
of planes

Vacancy

- **Self-Interstitials**:

  -"extra" atoms positioned between atomic sites.



distortion
of planes

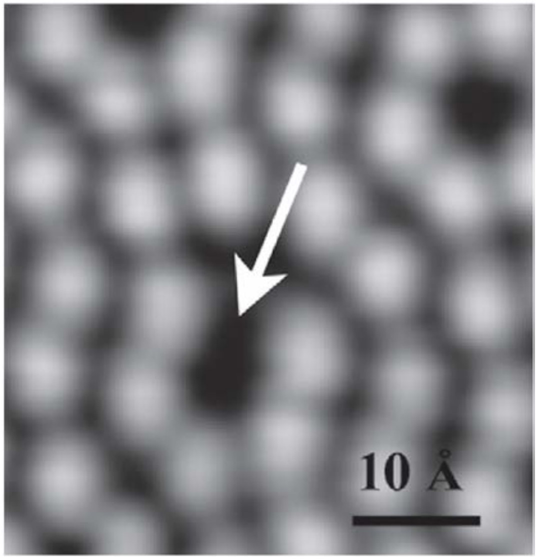
self-
interstitial

# VACANCY

**Vacancy** - Missing atom from lattice site.

Sometimes produced during solidification, sometimes by physical factors, (heating, neutrons, working) but present in all crystals.

Usually low in number, but reaches 1 vacancy per 10,000 atoms as temperature rises to melting point.



Vacancy on silicon surface

# Equilibrium Concentration of Point Defects

- Equilibrium concentration varies with temperature!

No. of defects

Activation energy

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

No. of potential defect sites.

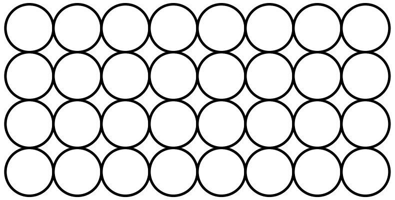
Temperature

Boltzmann's constant

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

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

(depending on units)



Each lattice site is a potential vacancy site

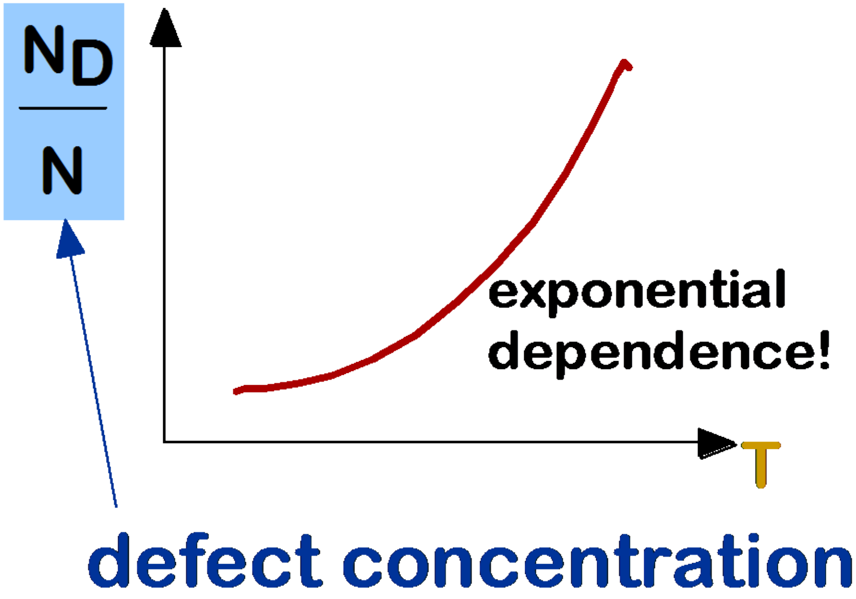
# MEASURING ACTIVATION ENERGY, $Q_D$

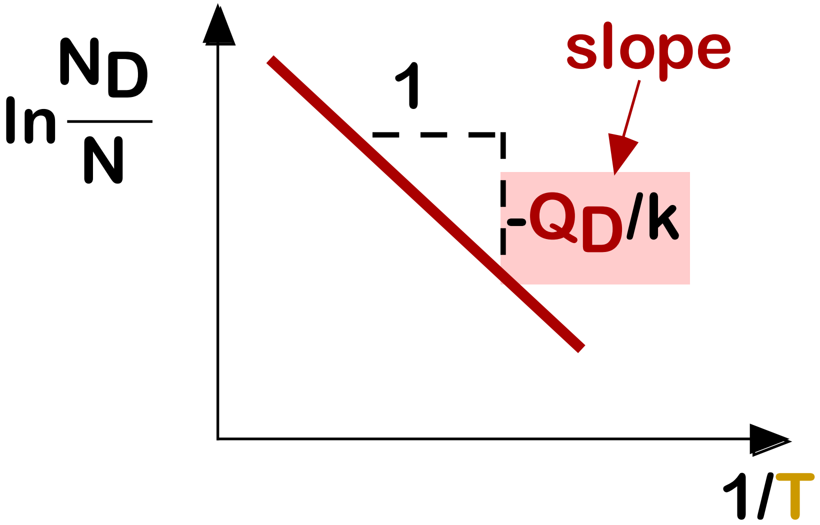
We can get Q from an experiment; taking natural logs of both sides….

.

$$\frac{N_D}{N} = \exp\left(\frac{-Q_D}{kT}\right) \longrightarrow \ln\left[\frac{N_D}{N}\right] = -\frac{Q_D}{k}\frac{1}{T}$$

- Measure $N_D$ as a function of T. Then: $\text{Plot } \ln\left[\frac{N_D}{N}\right] \text{ versus } \frac{1}{T}$





# ESTIMATING VACANCY CONC.

- Find the equil. # of vacancies in 1m$^3$ of Cu at 1000°C.
- 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/mole

0.9eV/atom

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

1273K

8.62 x 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:

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

# IMPURITIES IN SOLIDS

Pure metals are difficult to make and not often used.

Gold (is usually alloyed with Cu, Ni, Pt)

24 carat gold = 99.98%-99.95% gold, thus 14 carat = 14/24th

Copper (99.99%) is used for for electronics as impurities reduce electrical conductivity.

Pure Platinum is used for thermo-electric applications.

Usually engineering metals are combined with other metals or elements to give **ALLOYS**. (increased strength, corrosion resistance etc.)

e.g.

**STEEL** → Iron (Fe) + Carbon (C)

**BRASS** → Cu + Zn (zinc)

**BRONZE** → Cu + Sn (tin)

**TITANIUM Alloy** → Ti + 4 Al + 6 V (vanadium)

**Ni-Based SUPERALLOYS** → up to 10 elements

# SOLID SOLUTIONS

Simplest alloy is a **SOLID SOLUTION**.

Atoms of Element B are dissolved randomly into Element A (host) usually when they are in the liquid state.

"SOLVENT" - major element (host)

"SOLUTE" - minor element (impurity)

After freezing, they now form a **Solid Solution**.

One phase (all crystals/grains are the same as the next except for orientation i.e. same composition).

e.g.. Liquid solutions - water + alcohol

We can have both:

**SUBSTITUTIONAL AND INTERSTITIAL SOLID SOLUTIONS**

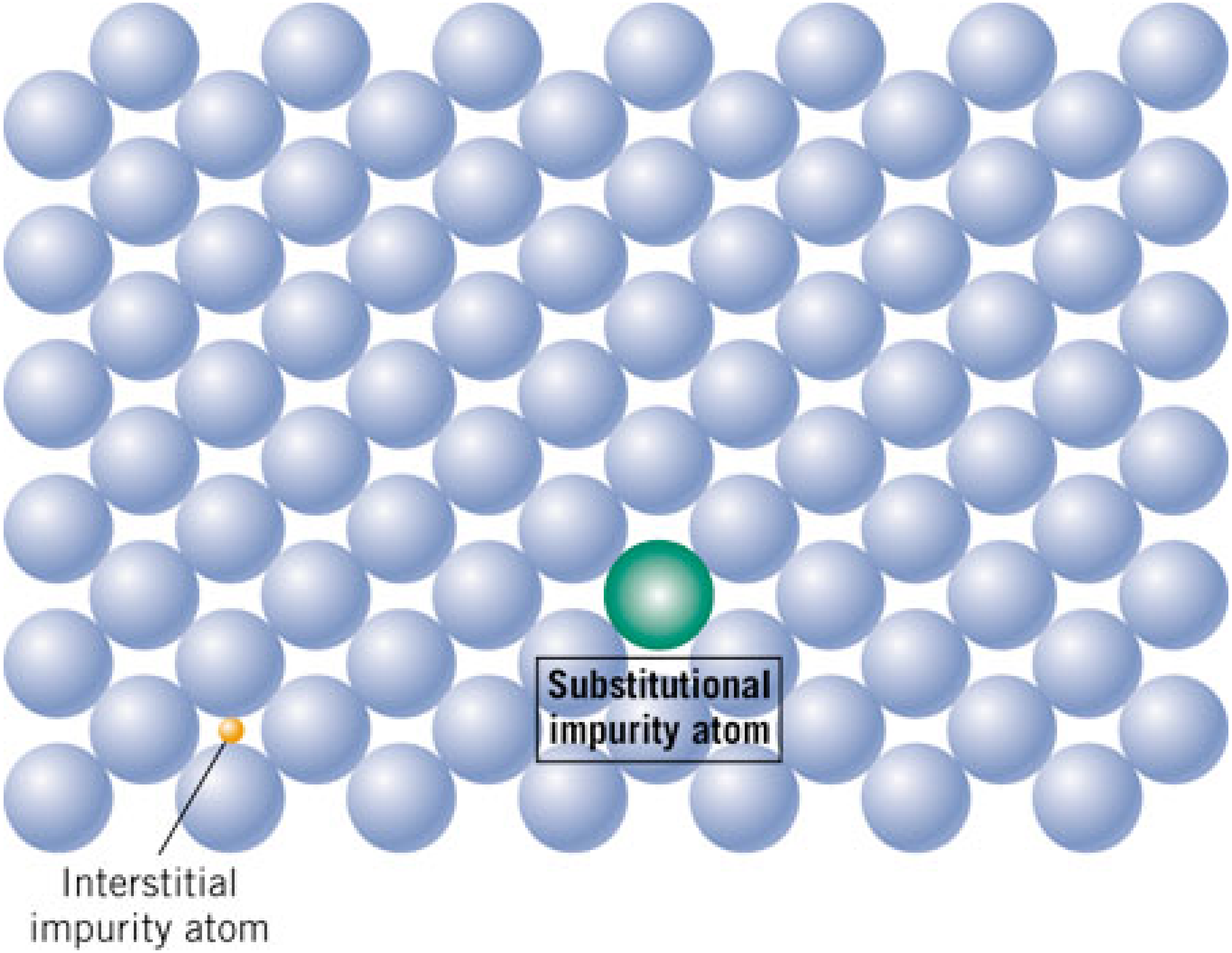
## SUBSTITUTIONAL SOLID SOLUTIONS

A host atom is replaced by a different type of atom. The substitutional atom can be either larger or smaller than the host atom but occupies its position. Causes a distortion to surrounding lattice.

## INTERSTITIAL SOLID SOLUTIONS

Impurity atoms go into spaces (interstices) between host atoms. Usually spaces are small so interstitial atoms have to be small.

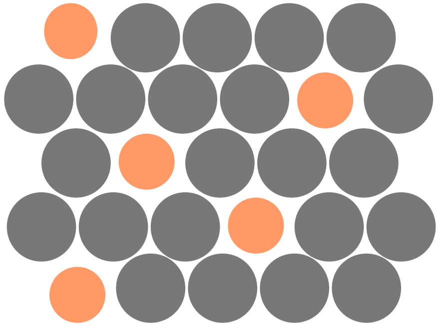
E.g. Hydrogen atoms in iron (from poor welding) - bad
Carbon atoms in iron – deliberate – to produce steel.


Substitutional impurity atom
Interstitial impurity atom

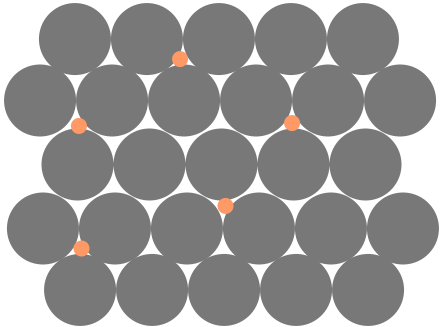
# Point Defects in Alloys

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

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



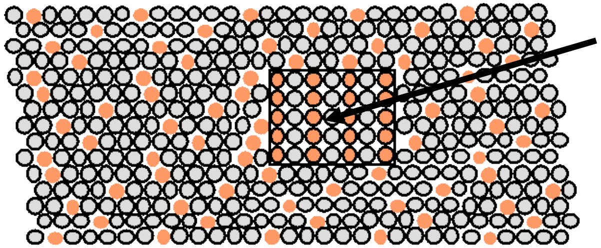
OR



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

Interstitial solid soln.
(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.

## COMPOSITIONS

In industry usually use weight% for alloys: easier to add 5 kgs of Mg to 10 tonnes of Aluminum than add 4 million atoms of Mg to 67 billion atoms of Al.

$$C_1 = \frac{m_1}{m_1 + m_2} x100$$

C1 is the wt% of element 1 where $m_1$ and $m_2$ are the weights of elements 1 and 2.

For chemical/scientific measures often need **atomic %.**

$$C_1' = \frac{n_{m1}}{n_{m1} + n_{m2}} x100 \qquad n_{m1} = \frac{m_1'}{A_1}$$

(g/g.mol$^{-1}$) → mol.

$n_{m1}$ is the number of moles of element 1, $m'_1$ is the mass (grams) and $A_1$ is the atomic weight of element 1 (g/mole) etc.

# Imperfections in Solids

Conditions for substitutional solid solution (S.S.)

- W. Hume – Rothery rules
  1. $\Delta r$ (atomic radius) < 15%
  2. Proximity in periodic table
     - i.e., similar electronegativities
  3. Same crystal structure for pure metals
  4. Valency
     - All else being equal, a metal will have a greater tendency to dissolve a metal of higher valency than one of lower valency

A slight difference in size can be tolerated (a slight distortion to lattice), but there is a limit to this, e.g.

| | **Copper (FCC) -** | **Nickel (FCC)** | **Size%** |
|---|---|---|---|
| r = | 0.128 nm | 0.125 nm | 2.3% |

Similar electronegativites, valence: Cu: +1, (+2), Ni: +2.
**There is 100% solubility between Cu and Ni.**

Whereas for Copper and Lead system:

| | **Copper (FCC)** | **Lead (FCC)** | **Size%** |
|---|---|---|---|
| r = | 0.128 | 0.175 | 36.7 |

There is only 0.1% solubility (only 1 in 1000 atoms can be replaced)

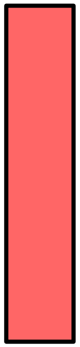
# Line Defects

**Dislocations:**

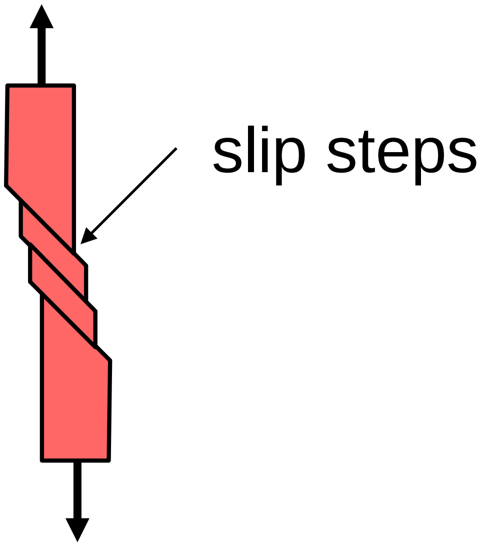
- are line defects,
- slip between crystal planes result when dislocations move,
- produce permanent (plastic) deformation.

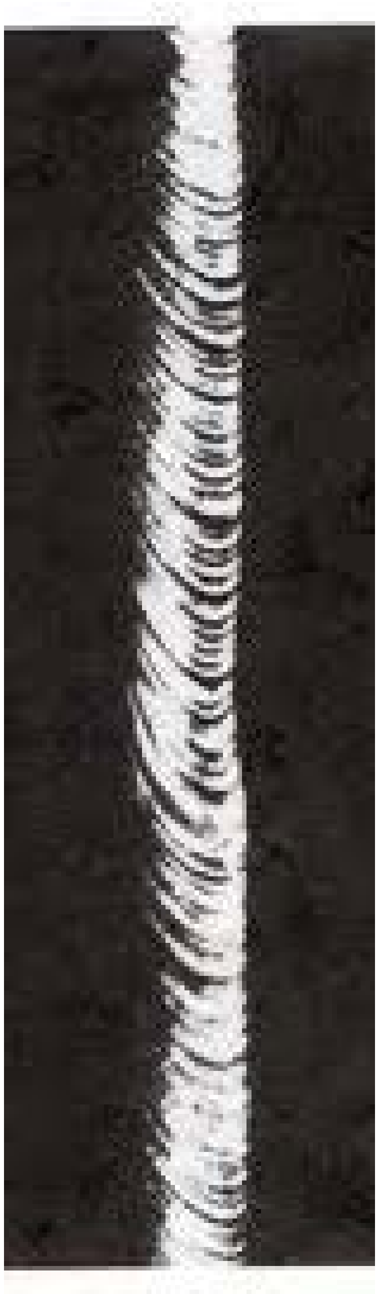
Schematic of Zinc (HCP):

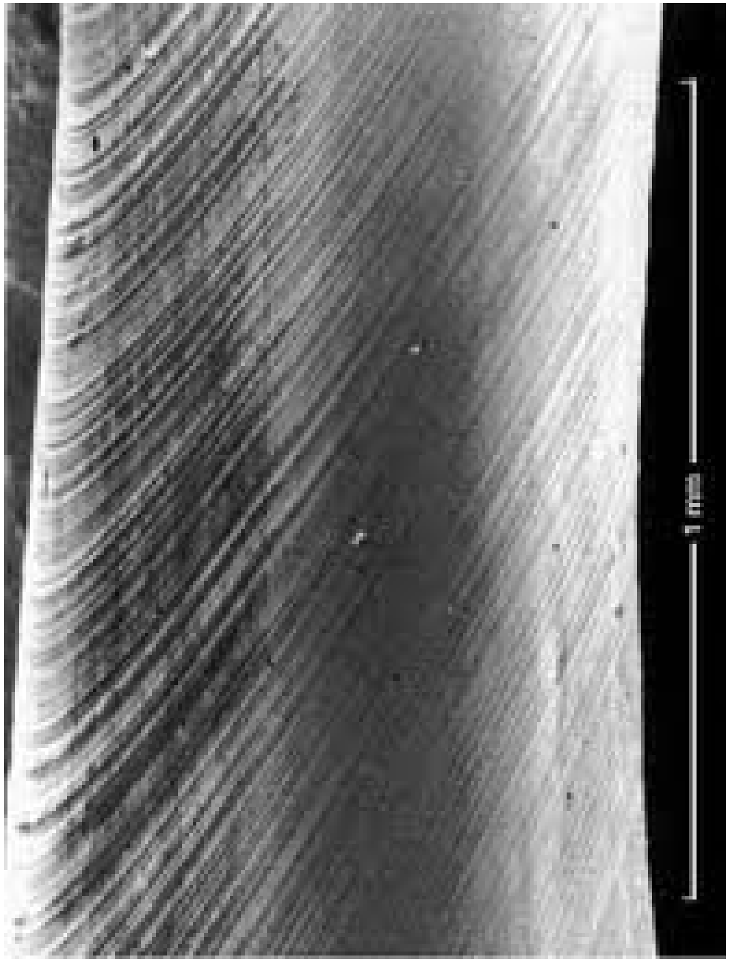
- before deformation



- after tensile elongation






1 mm

# Imperfections in Solids

Linear Defects (Dislocations)

- Are one-dimensional defects around which atoms are misaligned

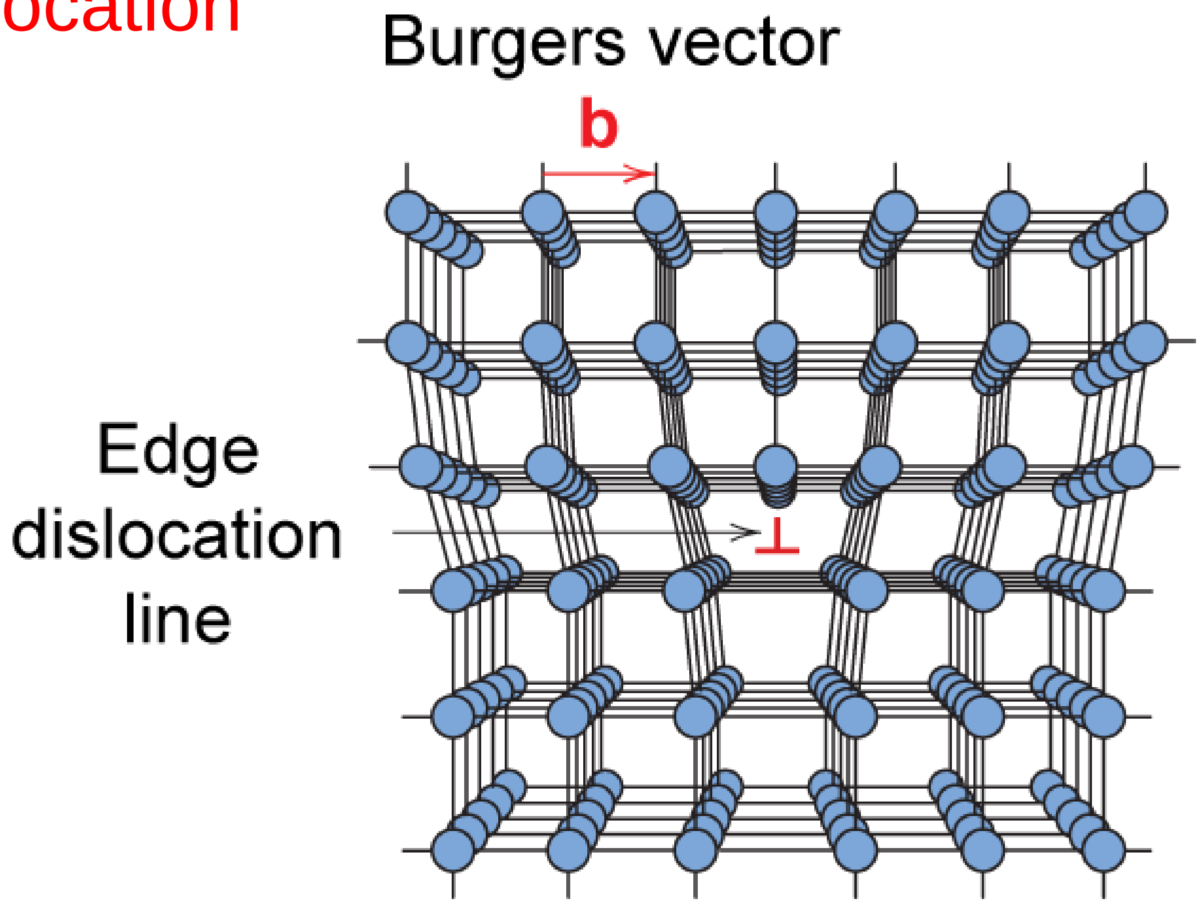
- **Edge dislocation**:
  - Looks like an extra half-plane of atoms have been inserted into a crystal structure
  - **b** ⊥ to dislocation line
- **Screw dislocation**:
  - spiral planar ramp resulting from shear deformation
  - **b** || to dislocation line

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

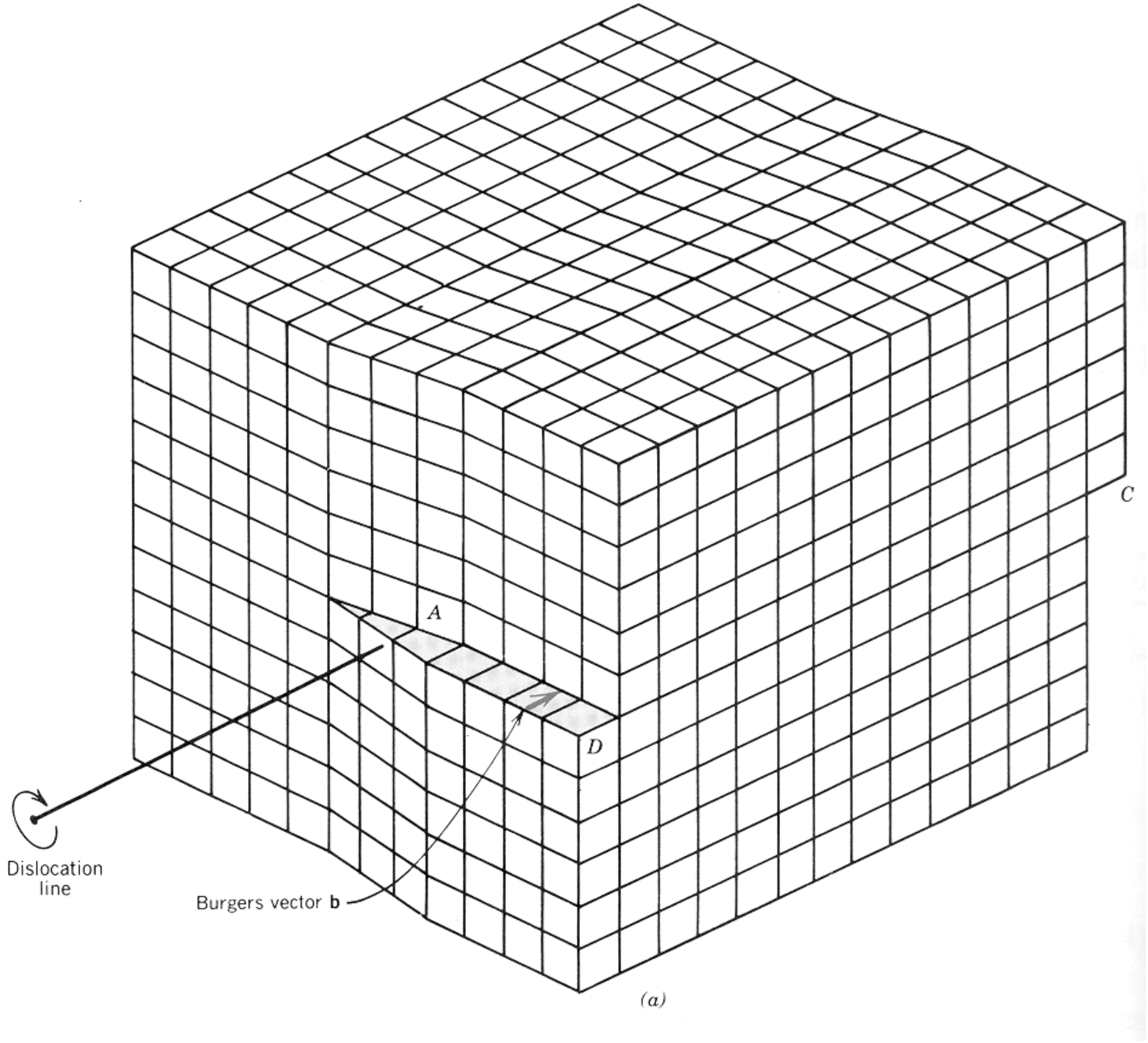
**Dislocations** make metals weaker than they should be, **BUT** also allow metals to be deformed (ie. allow plastic deformation). (Chp. 6)

# Imperfections in Solids

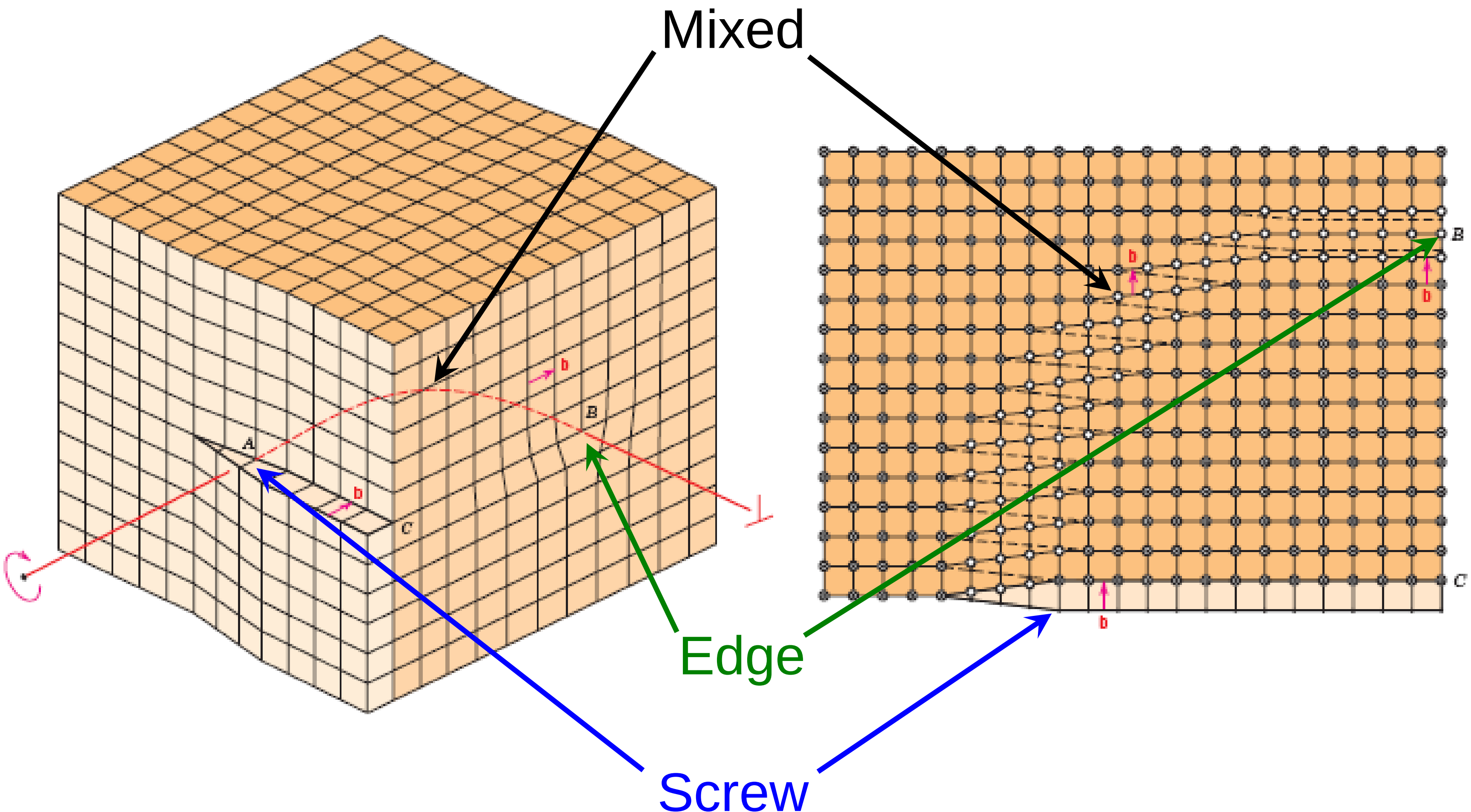
## Edge Dislocation



Screw Dislocation



# Edge, Screw, and Mixed Dislocations



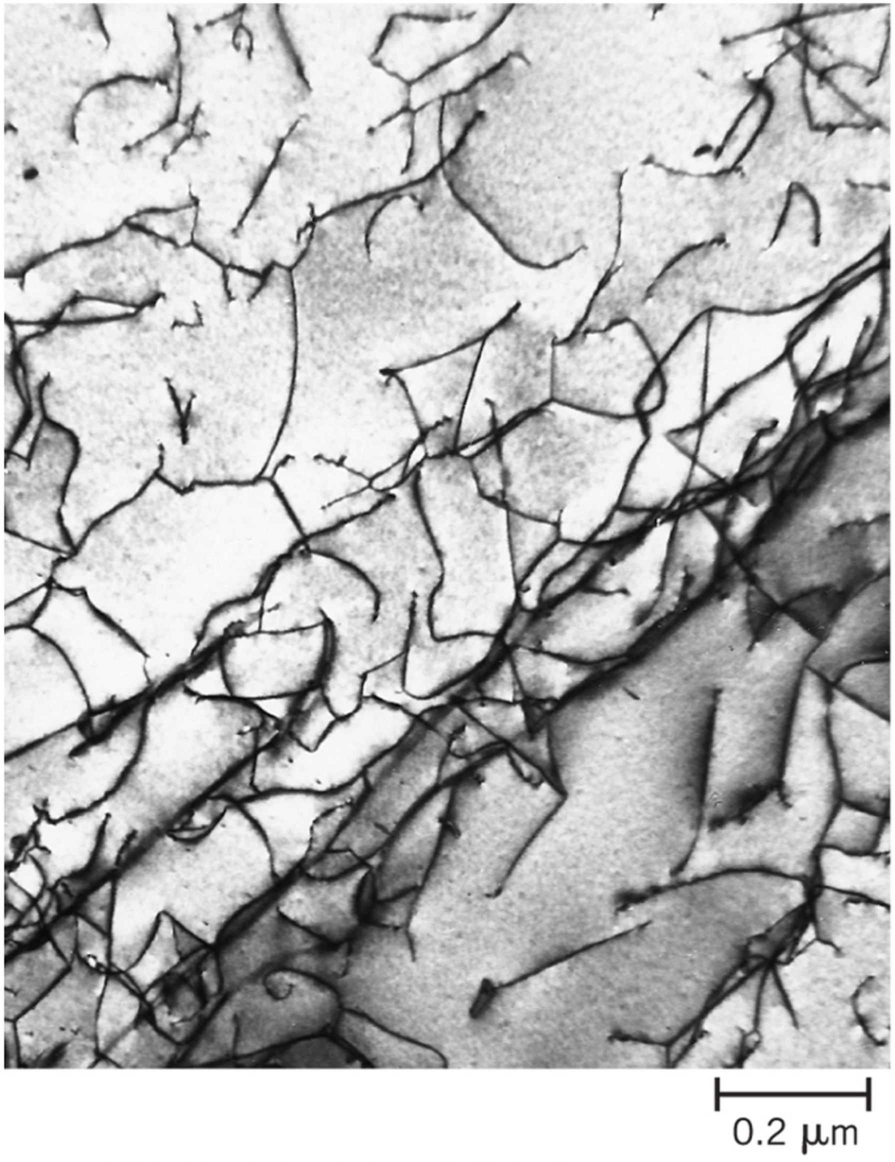
Mixed

Edge

Screw

Adapted from Fig. 4.5, *Callister 7e.*

# Imperfections in Solids

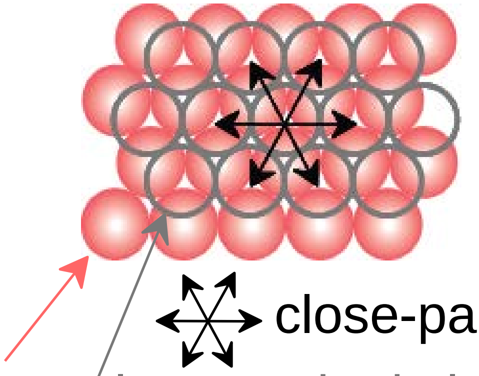


Courtesy of M. R. Plichta, Michigan Technological University.

Dislocations are visible in electron micrographs

# Dislocations & Crystal Structures

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



view onto two close-packed planes.

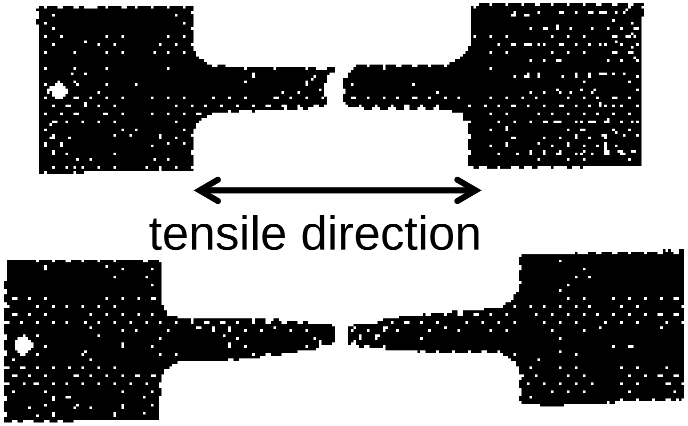
close-packed directions

close-packed plane (bottom)

close-packed plane (top)

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

- Specimens that were tensile tested.



Mg (HCP)

tensile direction

Al (FCC)

# INTERFACIAL DEFECTS

Defects between crystals or materials

## Surface Defects

Material surface: boundary between material and atmosphere. Atomic bonding disrupted. More reactive.

## Grain Boundaries (GBs)

Regions where grains (crystals) join. Because adjacent grains (crystals) have different orientations then some disorder at boundaries. Atomic bonding disrupted. GBs are more reactive chemically.

If a solid is made of only one crystal called: **Single Crystal**

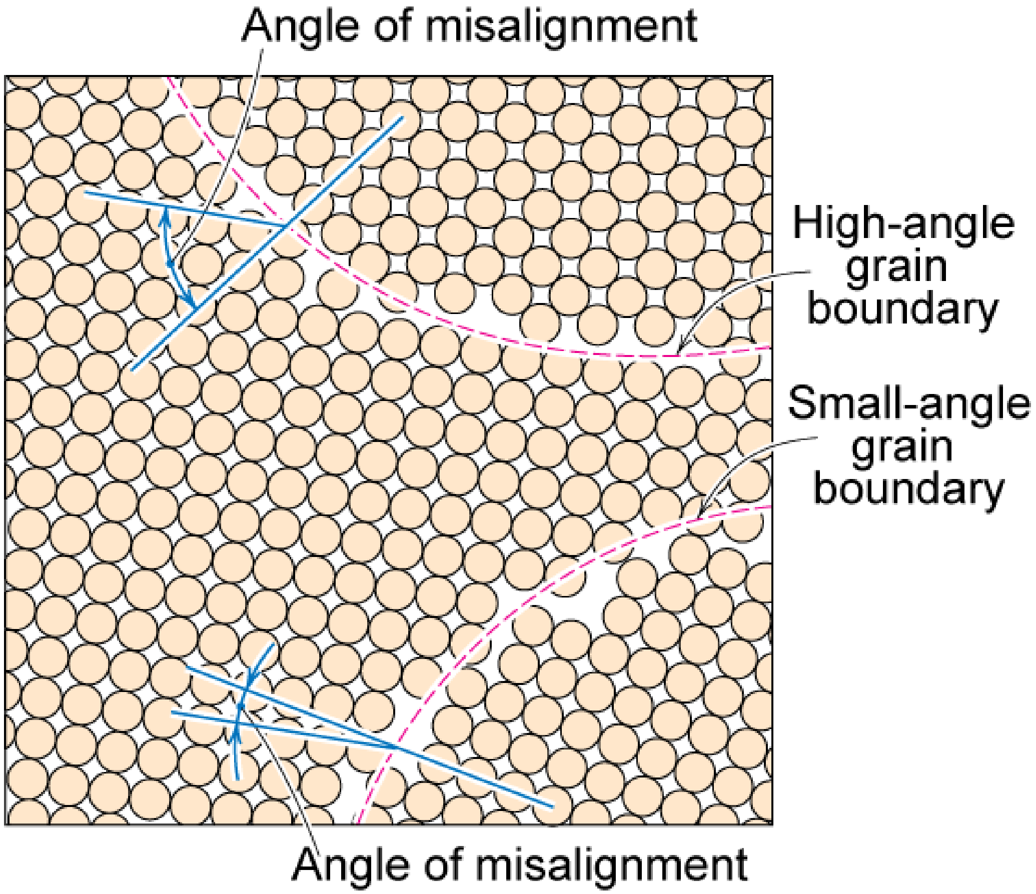
If solid has many Crystals → **Polycrystalline**.

Most materials/metals are **Polycrystalline.** i.e. composed of many crystals/grains joined together.

# Grain Boundaries in Polycrystalline Materials

## Grain Boundaries

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



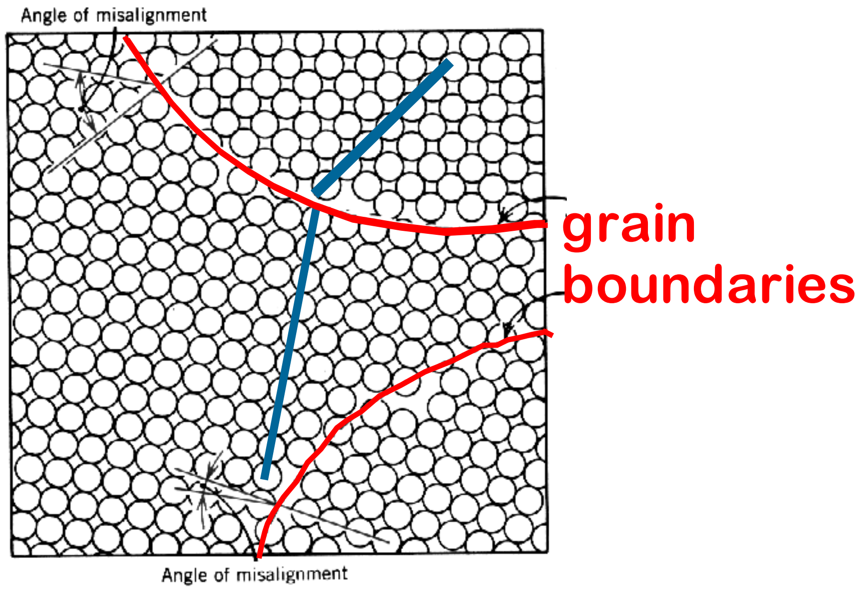
Notes# 4 - Mech 221 (adapted from Callister)

# GRAIN BOUNDARIES cont.

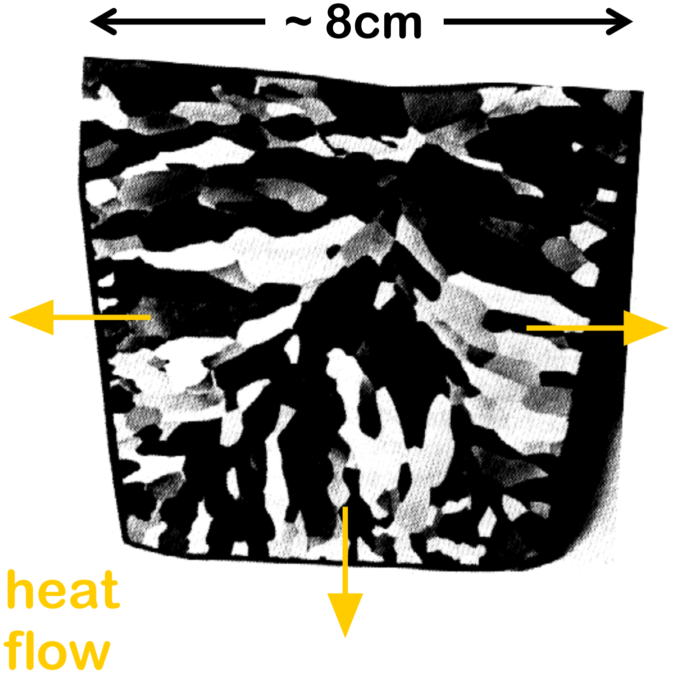
**Grain boundaries**:

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

## Schematic



## Metal Ingot



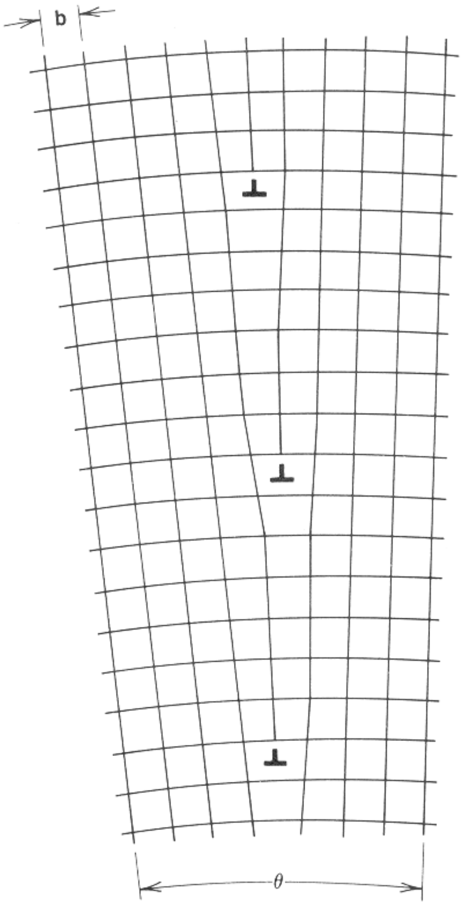


Figure 4.8 Demonstration of how a tilt boundary having an angle of misorientation θ results from an alignment of edge dislocations.

## BULK/VOLUME DEFECTS

Larger defects such as cracks, pores (holes), other stuff.

These are usually formed or introduced during casting or material fabrication.

They are not really seen as being part of the atomic or crystal structure but as defects introduced during a particular forming process, eg.

- Sand particles from a sand mould during sand-casting.
- Pores (holes/gas bubbles) formed during solidification of molten metal.
- Surface oxide trapped in metal when it is forged

# How to observe GRAINS and GRAIN BOUNDARIES

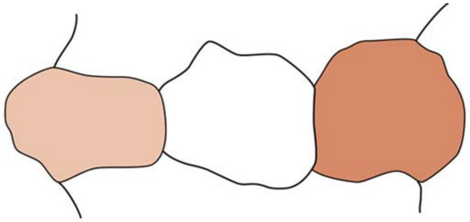
Grains, grain boundaries can be observed in metals/ceramics:

- Section (cut in half) and Grind sample.
- Polish (diamond paste).
- Etch (chemical attack) Occurs preferentially depending upon crystal orientation and in grain boundaries.
- View **MICROSTRUCTURE** with microscope.

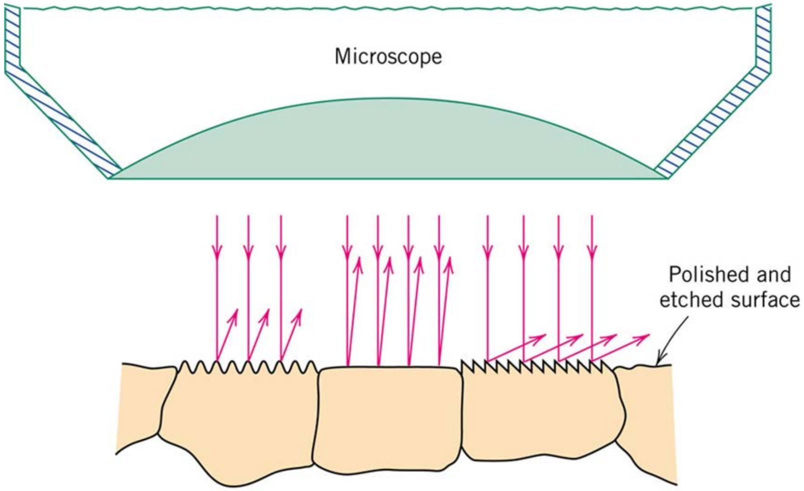
Can also use: Scanning Electron Microscope, SEM
Can measure properties such as **GRAIN SIZE**. This effects strength, toughness etc.

# OPTICAL MICROSCOPY

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



(a)



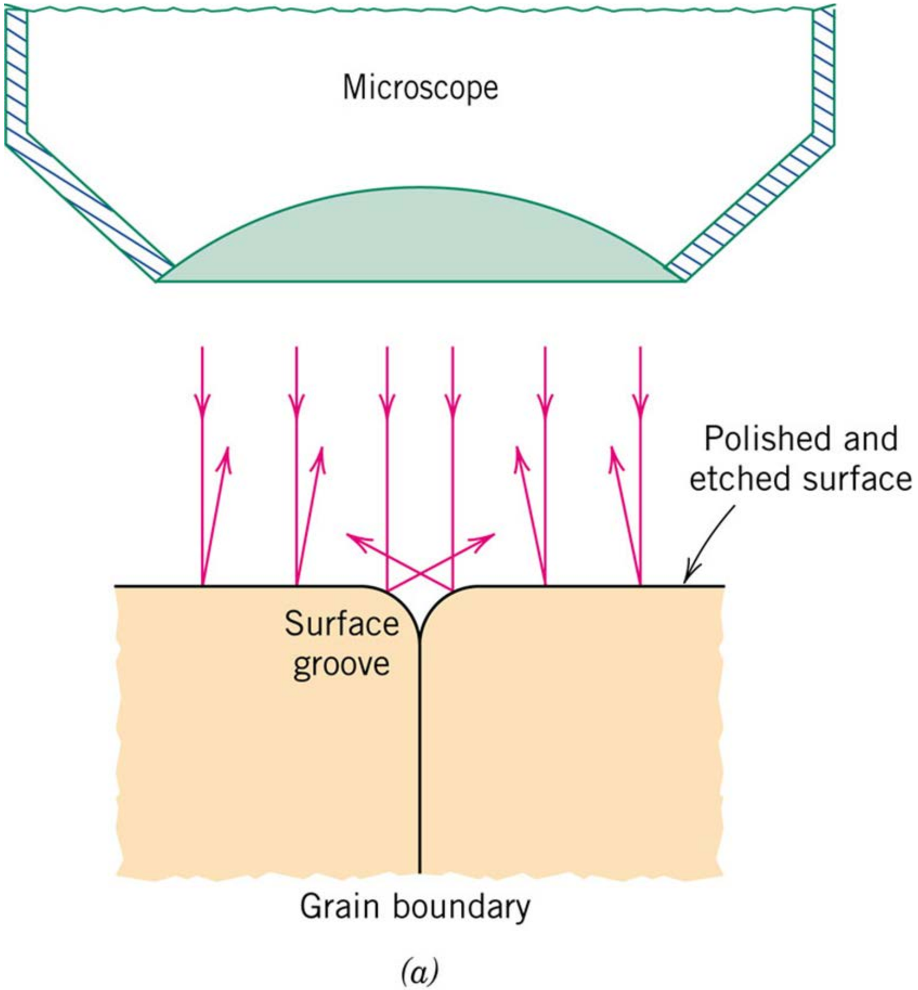
(b)

(c)

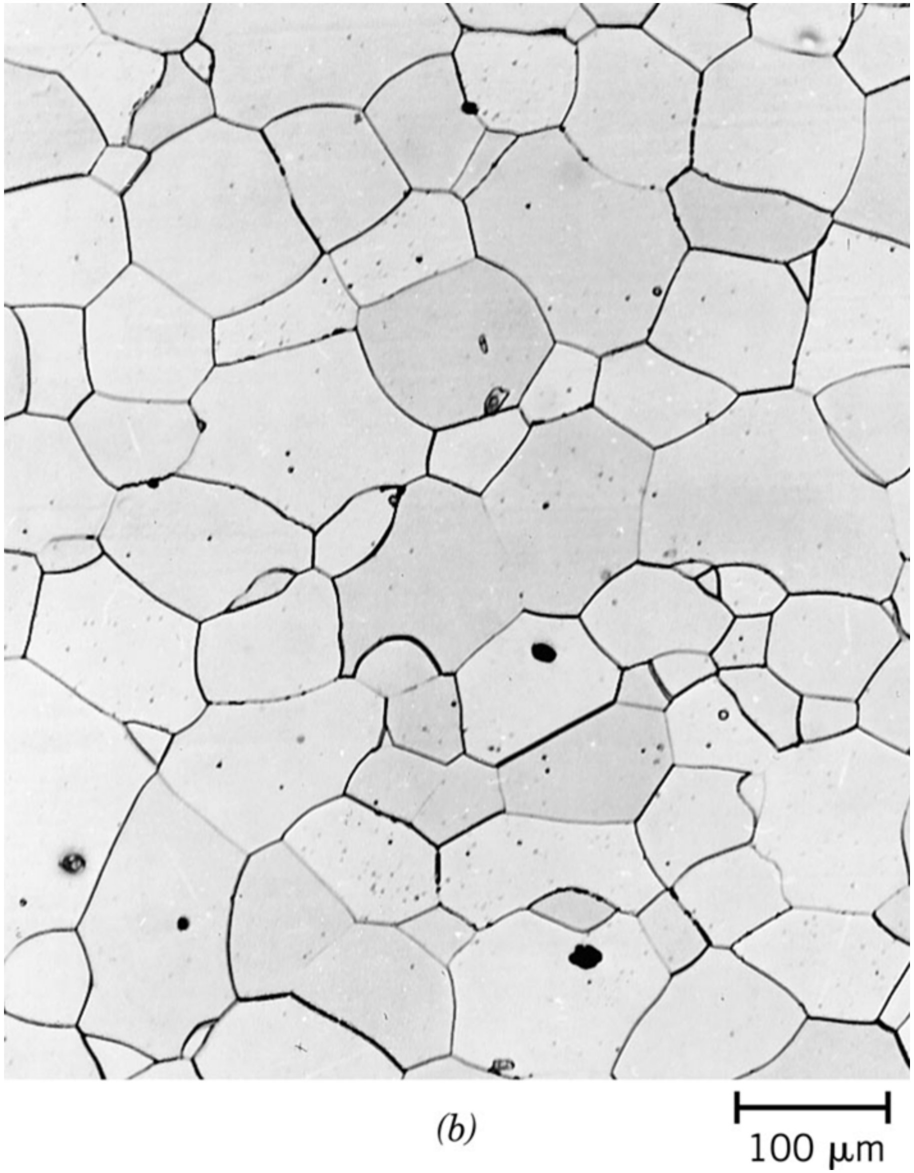
**micrograph of Brass (Cu and Zn)**

# Grain boundaries...

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



# Fe-Cr alloy



# Grain Size Determination

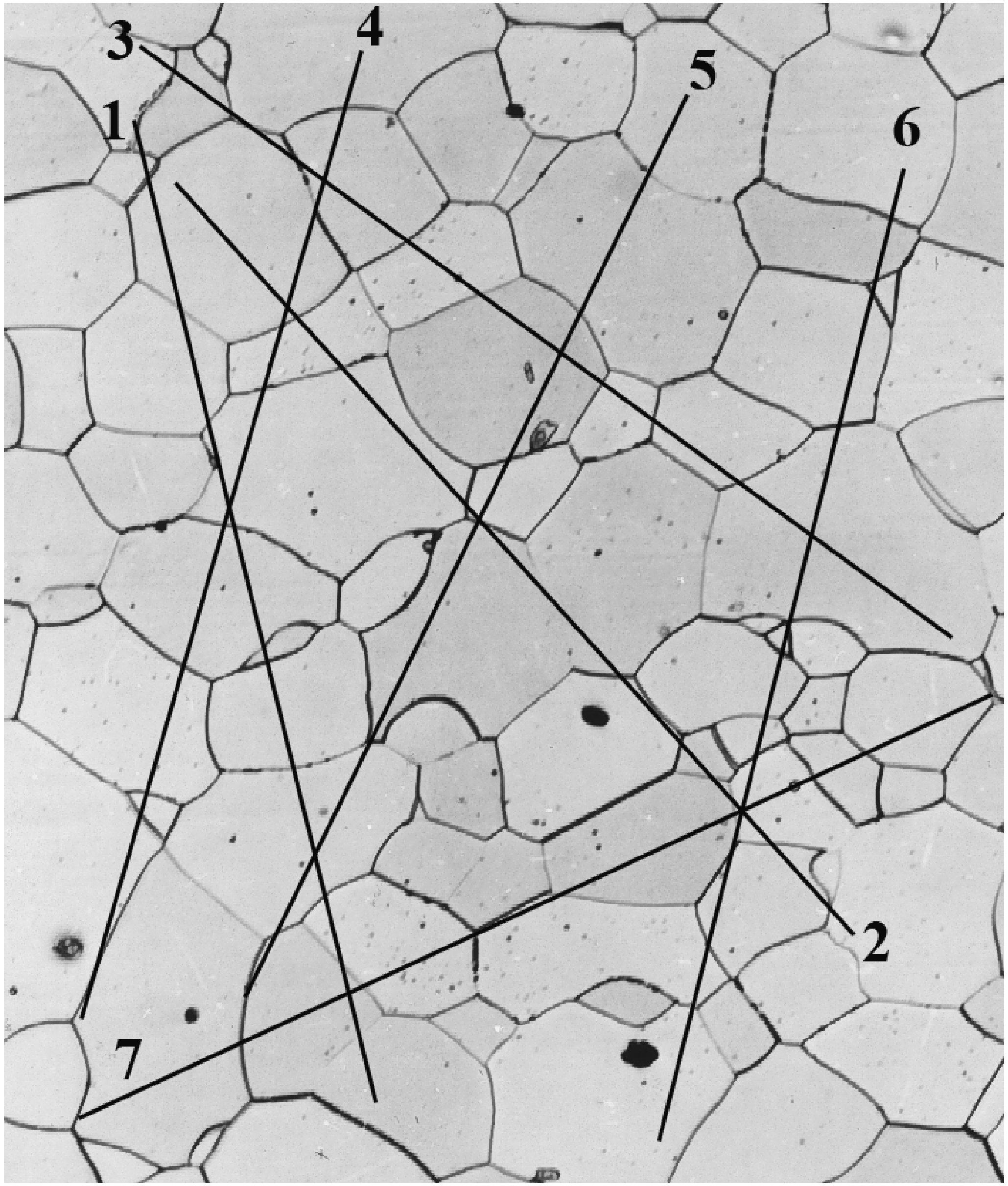
Grain size in metals can affect several mechanical properties especially strength. Can measure grain size by:

## Intercept method:

- Draw equal length lines randomly across photomicrograph. ($l$)
- Count number of grains intercepted per line. ($\mathbf{n_g}$)
- Line length is divided by average no. of grains per line ($l$ /$\mathbf{n_g}$)
- This is then divided by magnification of photo to give average grain diameter. ($l$ /$n_g$)/M = Avg. g.d.

$$\text{Average grain diameter} = \frac{l}{n_g M}$$

Photomicrograph Mag: 100X
7 randomly oriented straight lines labeled, (60 mm long)



| Line | No. of grains intersected |
|---|---|
| 1 | 11 |
| 2 | 10 |
| 3 | 9 |
| 4 | 8.5 |
| 5 | 7 |
| 6 | 10 |
| 7 | 8 |
| AVG | 9.1 |

Avg. Grain Dia. = $(l / n_g)/M$

$(60 / 9.1)/100 = 6.59 \times 10^{-2}$mm

# Grain Size (cont)

- **ASTM Grain size Number (n)**
- Take photo at 100X and compare with ASTM standard charts of grain size. Each chart shows particular grain size (n). As n increases, grain size decreases. Select chart that is closest match to actual structure.

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

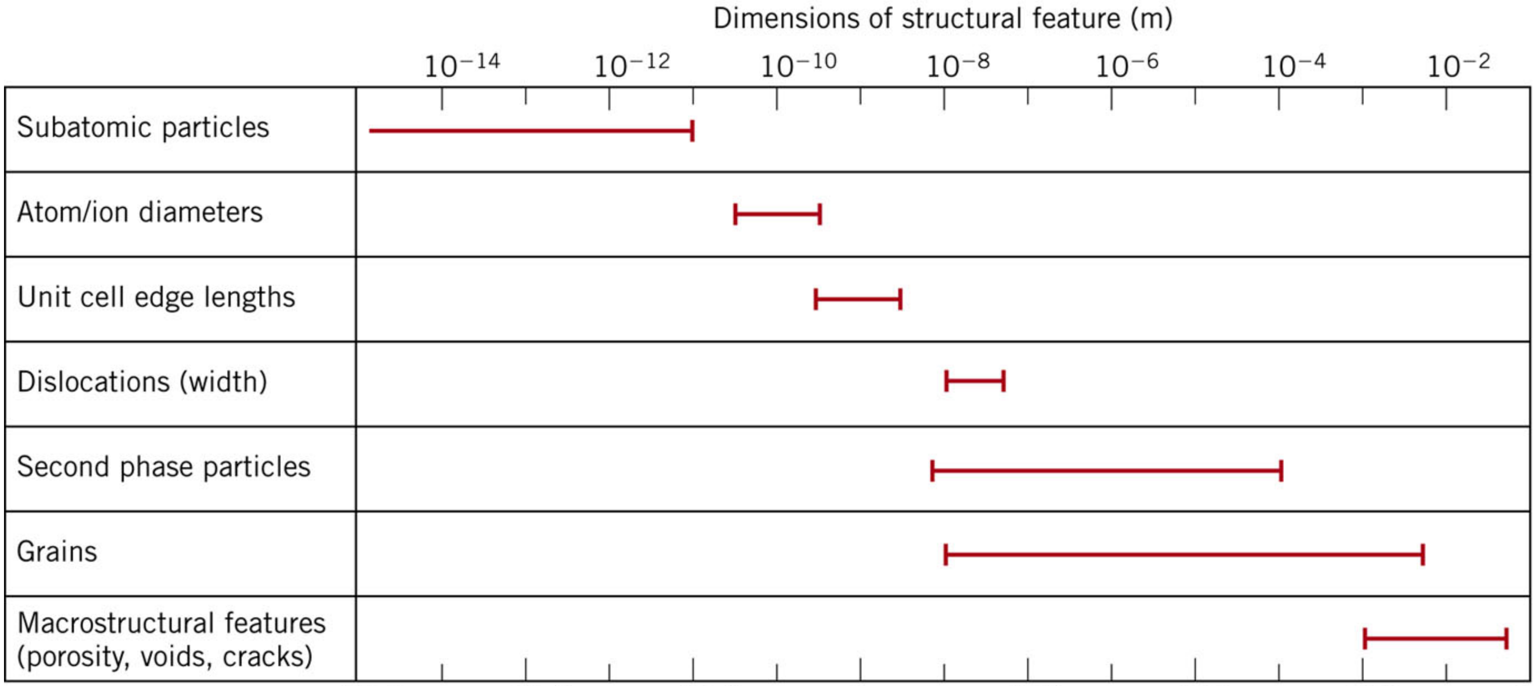
- where N is the average number of grains per square inch at Magnification X100
- n = ASTM grain size number

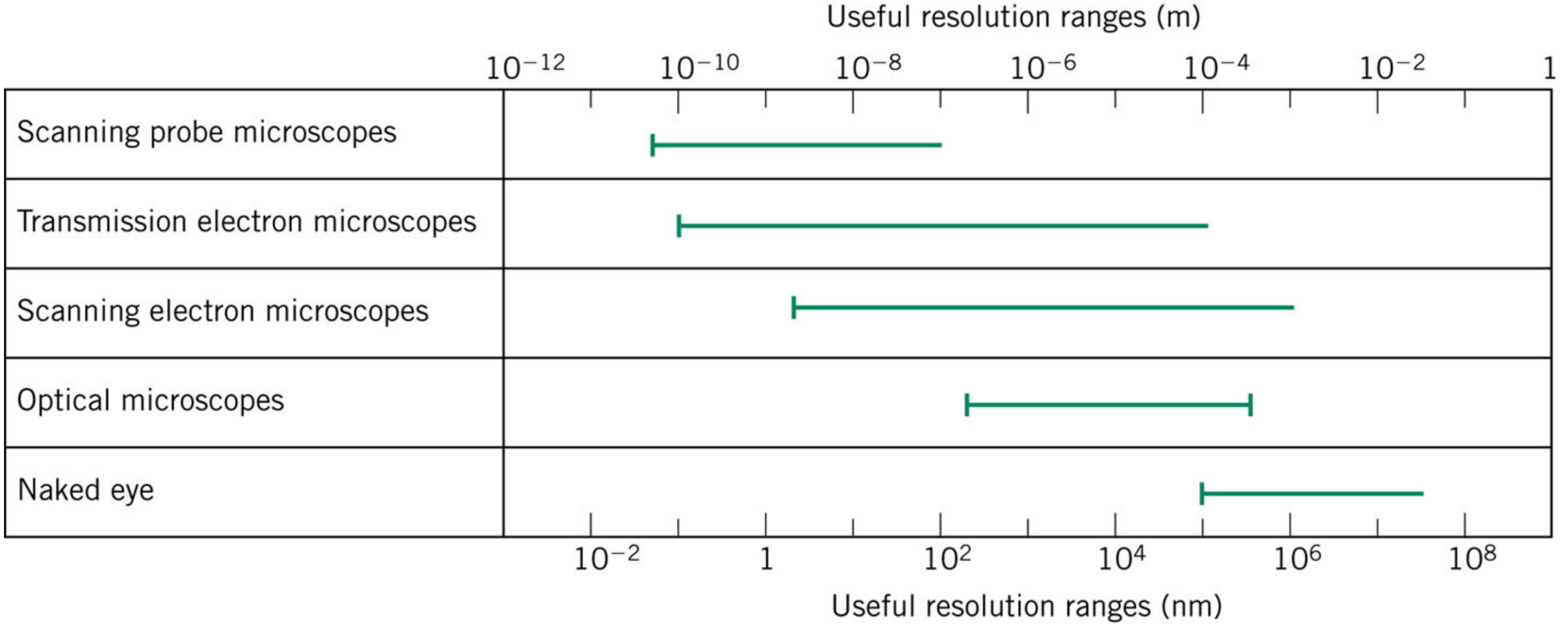
# Microscopy

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

For higher resolution need higher frequency

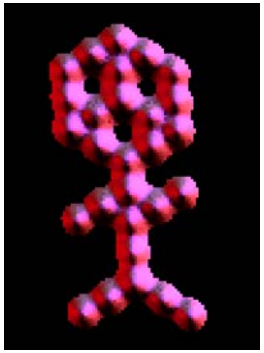
- X-Rays? Difficult to focus.
- Electrons
  - wavelengths ca. 3 pm (0.003 nm)
    (Magnification - 1,000,000X)
  - Atomic resolution possible
  - Electron beam focused by magnetic lenses

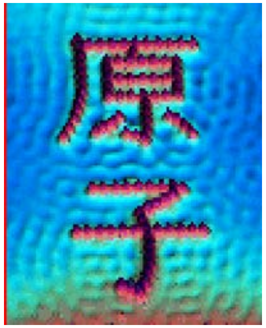

Dimensions of structural feature (m)
$10^{-14}$
$10^{-12}$
$10^{-10}$
$10^{-8}$
$10^{-6}$
$10^{-4}$
$10^{-2}$
Subatomic particles
Atom/ion diameters
Unit cell edge lengths
Dislocations (width)
Second phase particles
Grains
Macrostructural features (porosity, voids, cracks)


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
$10^{2}$
$10^{4}$
$10^{6}$
$10^{8}$
Useful resolution ranges (nm)

# Scanning Tunneling Microscopy (STM)

- Atoms can be arranged and imaged!





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

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

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

# SUMMARY

- **Point**, **Line**, and **Area** 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.)