

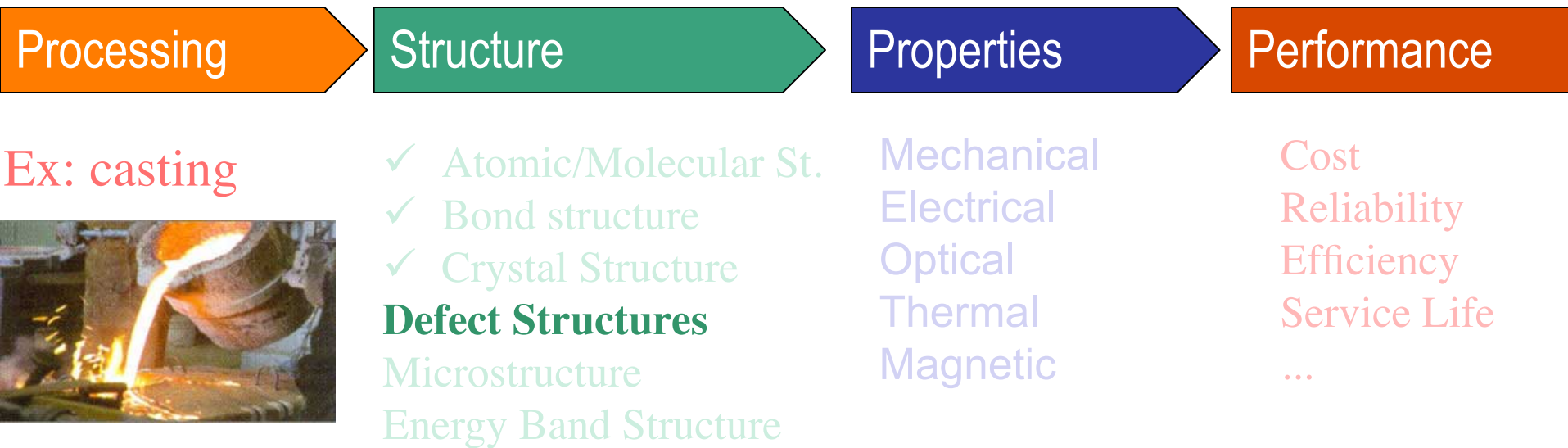
CHAPTER 4: IMPERFECTIONS IN SOLIDS

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?



Today's Agenda



Melt
↓
SOLIDIFICATION

Crystals as Building Blocks

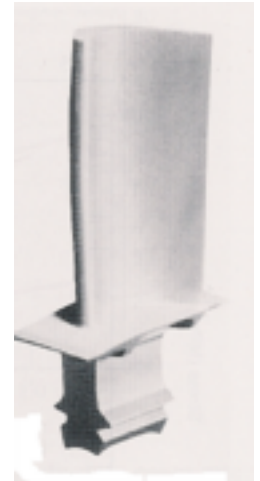
- Some engineering applications require single crystals:
 - diamond single crystals for abrasives
 - turbine blades



(Courtesy Martin Deakins, GE Superabrasives, Worthington, OH. Used with permission.)

- Properties of crystalline materials often related to crystal structure.
 - Ex: Quartz fractures more easily along some crystal planes than others.

Fig. 8.33(c), *Callister 7e*.
(Fig. 8.33(c) courtesy of Pratt and Whitney).



(Courtesy P.M. Anderson)

Polycrystals

- Most engineering materials are polycrystals.



Anisotropic

Properties vary with direction: anisotropic.

Adapted from Fig. K, color inset pages of *Callister 5e*.

(Fig. K is courtesy of Paul E. Danielson, Teledyne Wah Chang Albany)

Isotropic

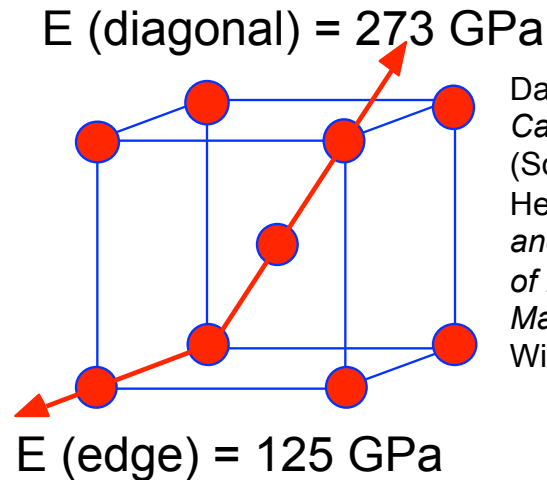
Properties are independent of direction: isotropic.

- Nb-Hf-W plate with an electron beam weld.
- Each "grain" is a single crystal.
- If grains are randomly oriented, overall component properties are not directional.
- Grain sizes typ. range from 1 nm to 2 cm (i.e., from a few to millions of atomic layers).

Single vs Polycrystals

- Single Crystals

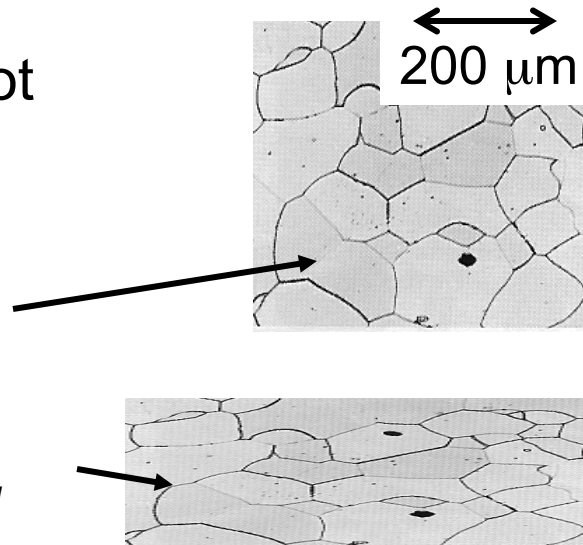
- Properties vary with direction: **anisotropic**.
- Example: the modulus of elasticity (E) in BCC iron:



Data from Table 3.3, *Callister 7e*.
(Source of data is R.W. Hertzberg, *Deformation and Fracture Mechanics of Engineering Materials*, 3rd ed., John Wiley and Sons, 1989.)

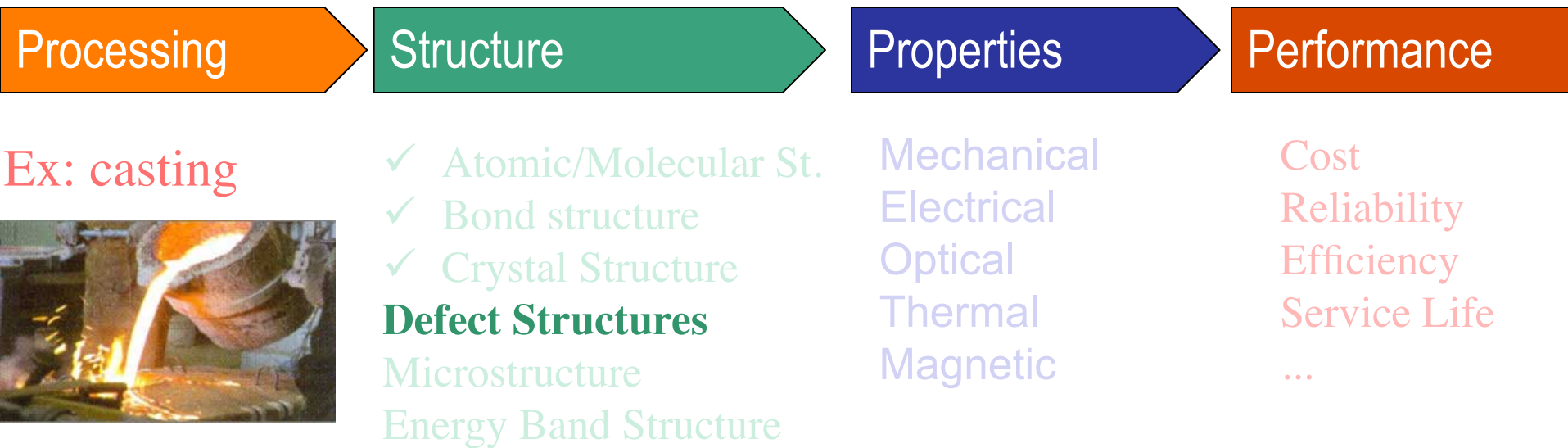
- Polycrystals

- Properties may/may not vary with direction.
- If grains are randomly oriented: **isotropic**.
($E_{\text{poly iron}} = 210$ GPa)
- If grains are **textured**, anisotropic. (*preferential crystallographic orientation*)



Adapted from Fig. 4.14 (b), *Callister 7e*.
(Fig. 4.14(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].)

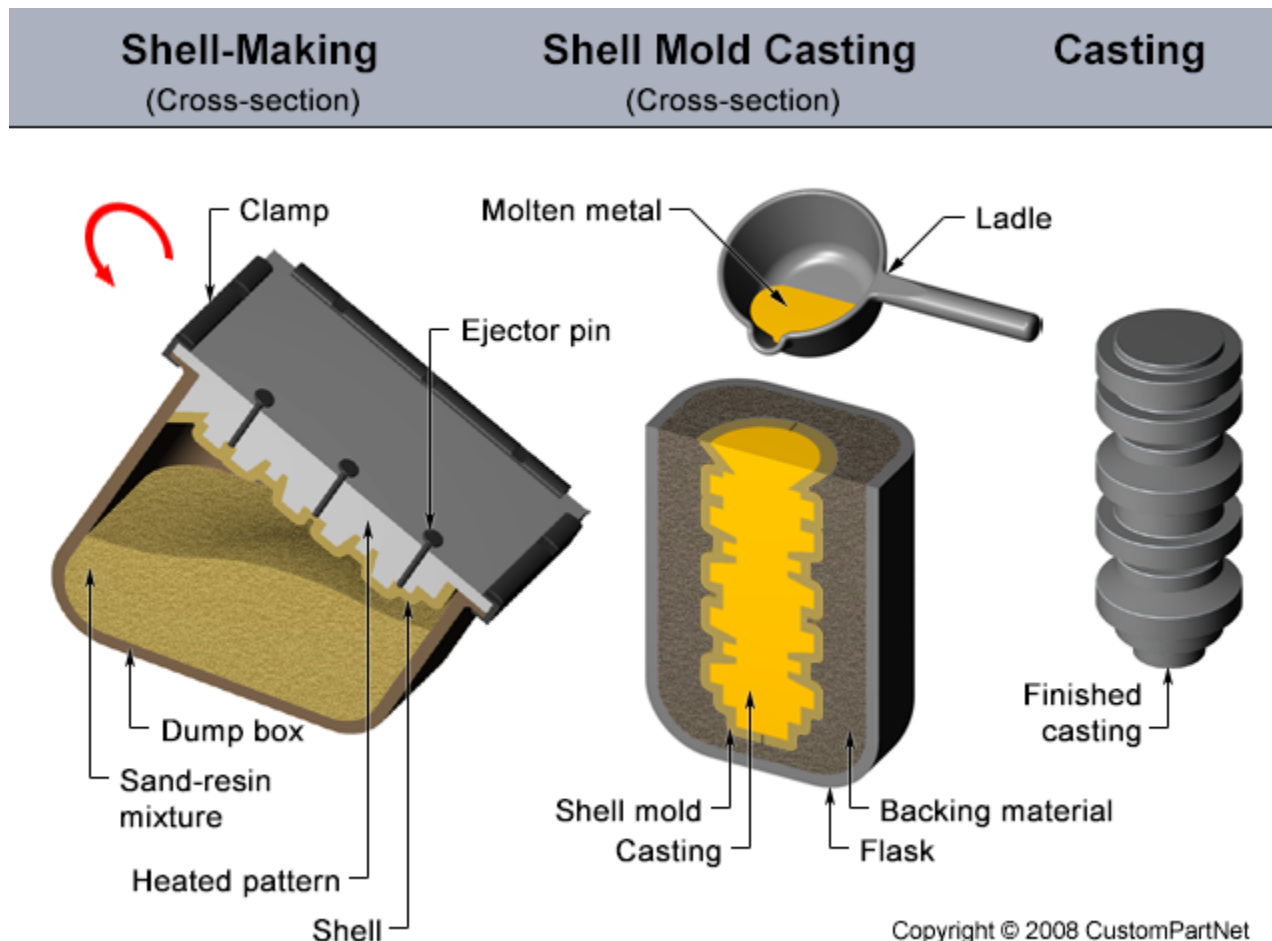
Today's Agenda



Melt
↓
SOLIDIFICATION

Solidification of Metals

- The solidification of metals and alloys is an important industrial process since most metals are melted and then cast into semifinished or finished shape.
- When molten alloys are cast, solidification starts at the walls of the mold

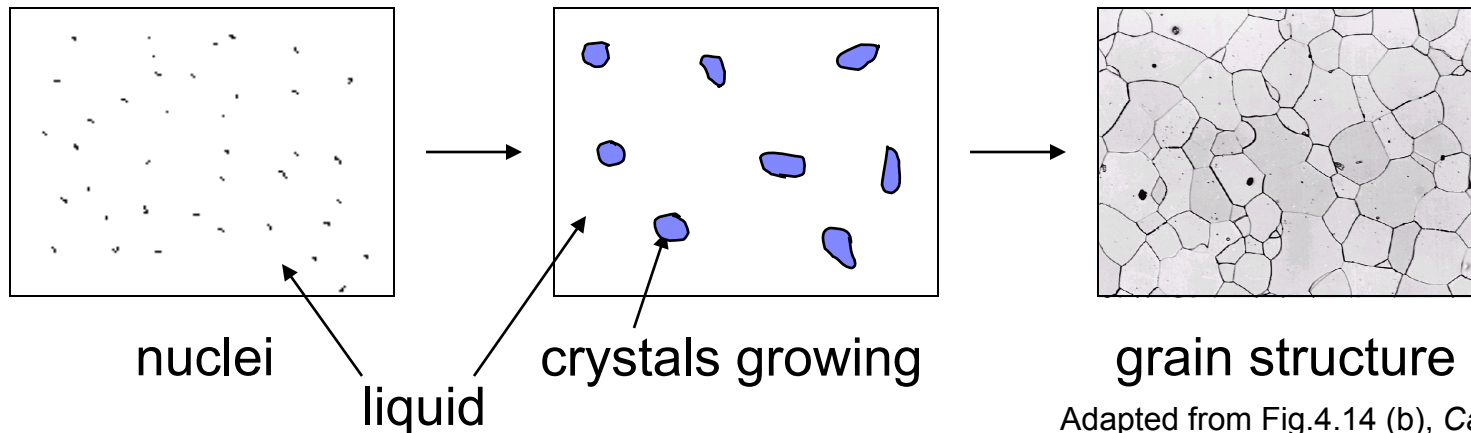


Imperfections in Solids

- **Solidification**- result of casting of molten material

Two steps of solidification:

1. **Nucleation:** Formation of stable nuclei in the melt
 2. **Growth:** Crystals grow until they meet each other
- Start with a molten material – all liquid



Adapted from Fig.4.14 (b), Callister 7e.

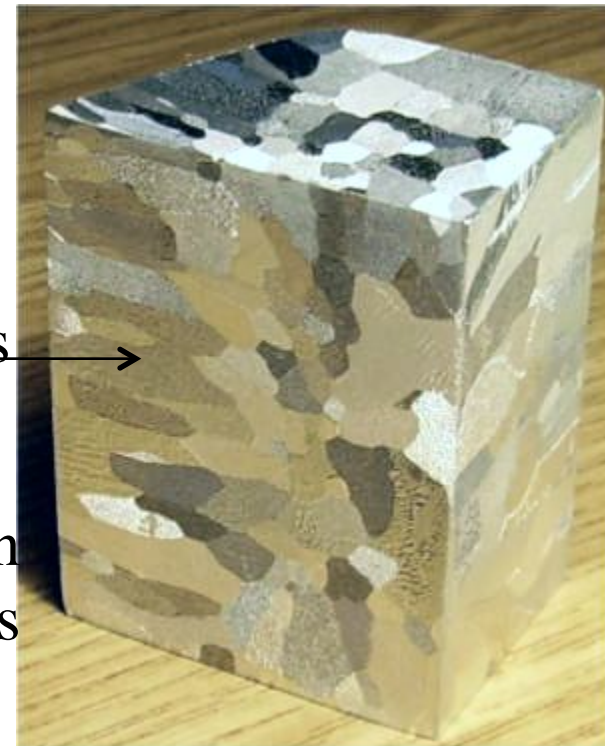
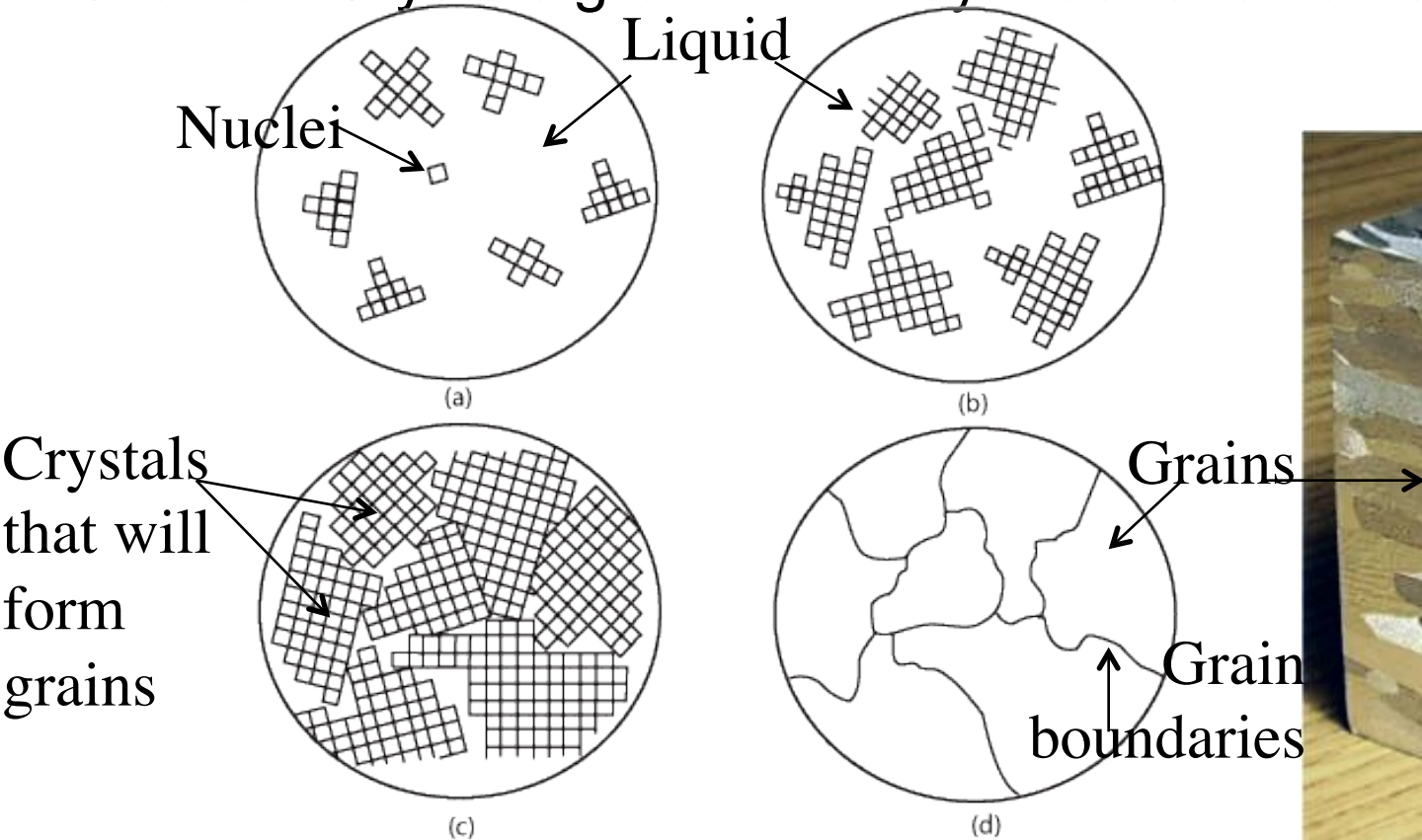
- Crystals grow until they meet each other

Solidification of Polycrystalline Material

- Almost all engineering crystalline materials are composed of many crystals.
- Two steps of solidification:

1. Nucleation: Formation of stable nuclei in the melt

2. Growth: Crystals grow until they meet each other



Solidification of Single Crystals

There are also materials that consist of only one crystal.

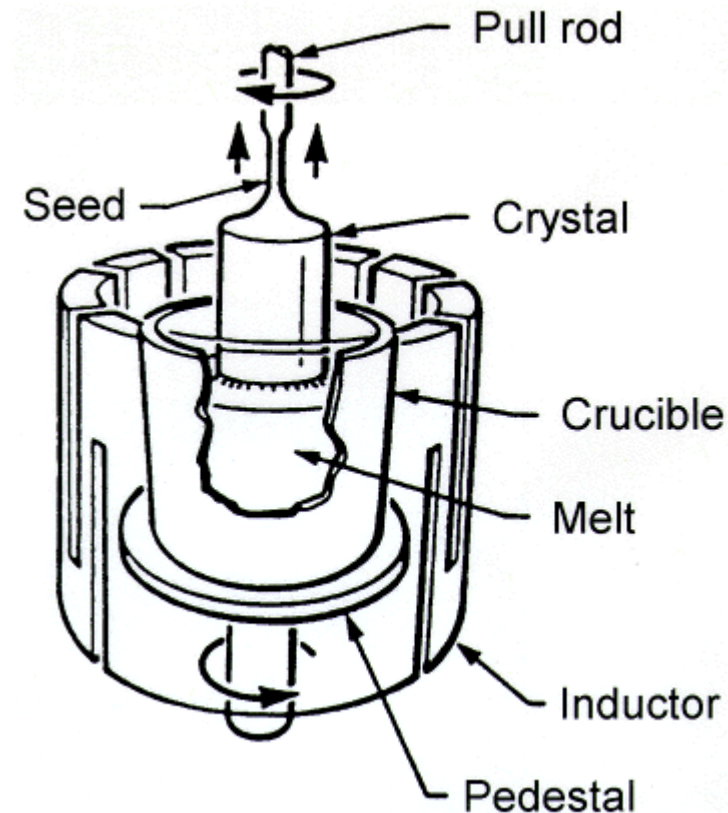
Examples:

- *High-temperature creep-resistant gas turbine blades*

(At high temperatures, grain boundaries become weaker than the grain bodies)

- *Silicon single crystals for semiconductor devices.*

(Grain boundaries would disrupt the flow of electrons in devices)

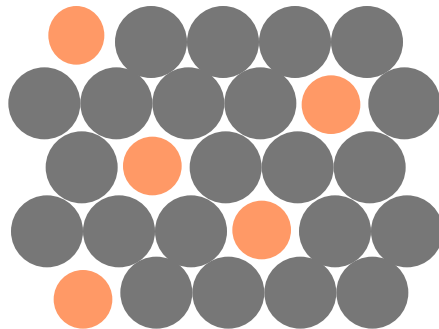


Metallic Solid Solutions

- Most engineering metals are combined with other metals or non-metals to provide increased strength, higher corrosion resistance or other desired properties → «METAL ALLOY»
- Simplest type of alloy = Solid Solution: (addition of impurity atoms to a metal)

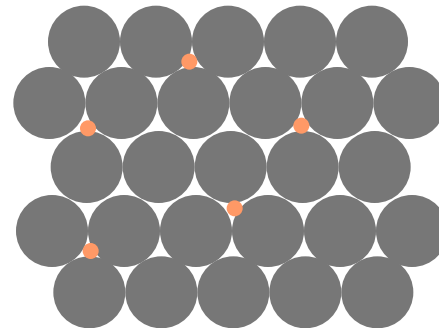
A solid that consists of two or more elements atomically dispersed in a **single-phase** structure. Two types of solid solutions:

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



OR

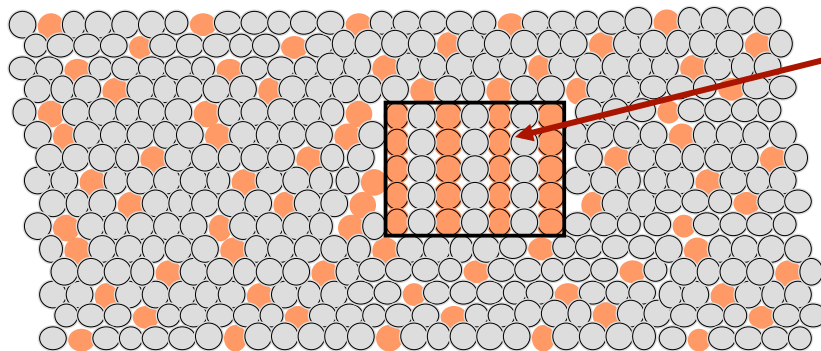
Interstitial alloy
(e.g., **C** in Fe)



Second Phase

- While solute atoms are being added, new compounds / structures may form beyond solubility limit, or solute forms local **PRECIPITATES**.
- Nature of the impurities, their concentration, reactivity, temperature and pressure, etc decides the formation of solid solution or a second phase.

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.

Imperfections in Solids

There is no such thing as a perfect crystal.

- What are these imperfections?

- Why are we interested

IMPERFECTIONS IN SOLIDS ?

“Crystals are like people, it is the defects in them which tend to make them interesting!” - Colin Humphreys.



Imperfections in Solids

Is it enough to know bonding and structure of materials to estimate their macro properties ?

BONDING
+
STRUCTURE

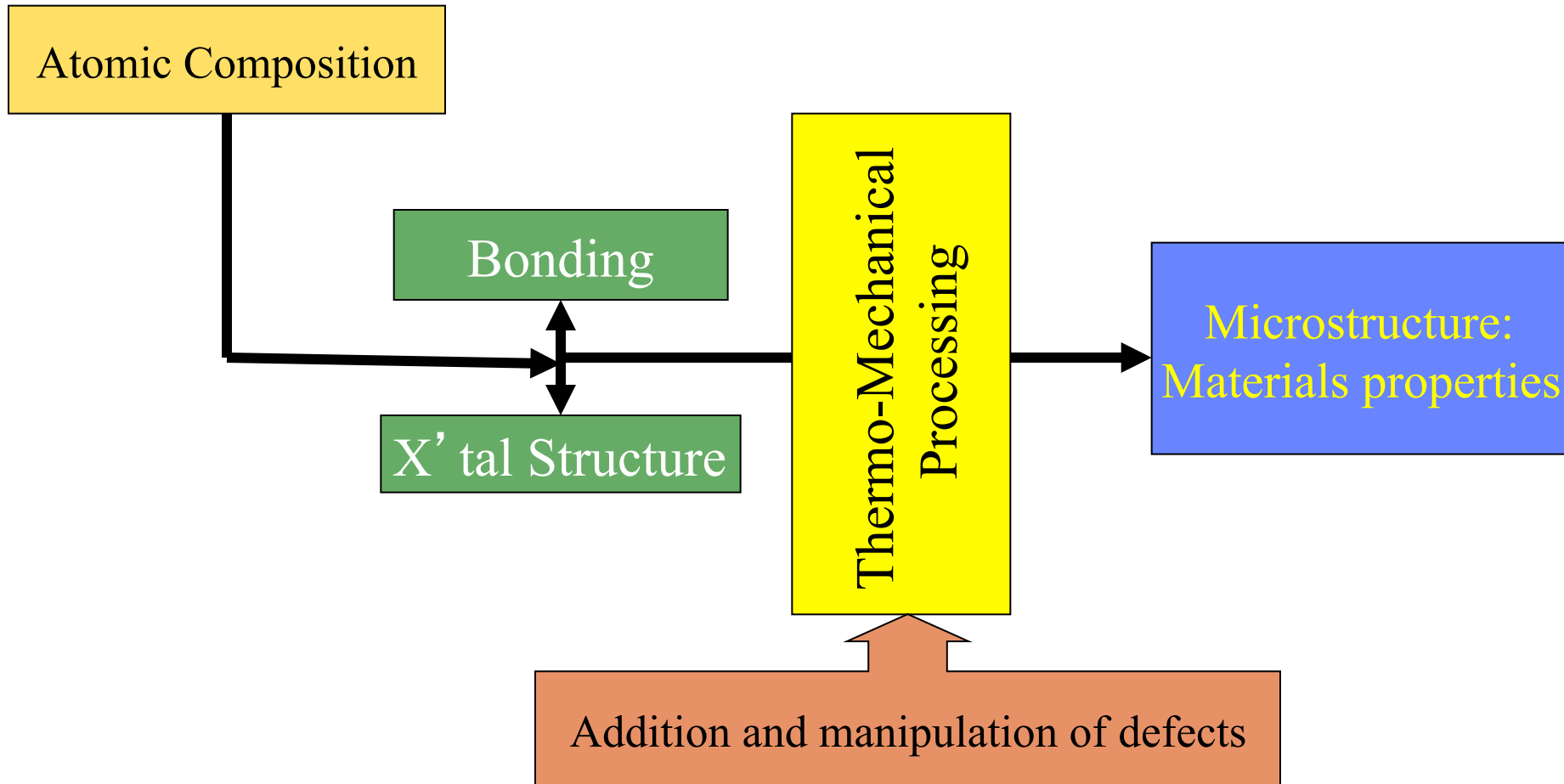
+
DEFECTS

PROPERTIES

Color/Price of Precious Stones
Mechanical Properties of Metals
Properties of Semiconductors
Corrosion of Metals

Many of the important properties of materials are due to the presence of imperfections.

Imperfections in Solids



Perfection...

In terms of:

1. Chemical composition – pure
 2. Atomic arrangement – defect free
- Both are critical in determining the performance of material.
 - Real engineering materials are not perfect.
 - Properties can be altered through defect engineering.



Types of Imperfections

- Vacancy atoms
- Interstitial atoms
- Substitutional atoms

Point defects

- Dislocations

Line defects

- Grain Boundaries

Area defects



Classification of Defects

The defects are classified on the basis of dimensionality:

- 0-dimensional: point defects
- 1-dimensional: line defects
- 2-dimensional: interfacial defects
- 3-dimensional: bulk defects



0 dim: Point Defects

- localized disruption in regularity of the lattice
- on and between lattice sites

3 Types:

1. Substitutional Impurity

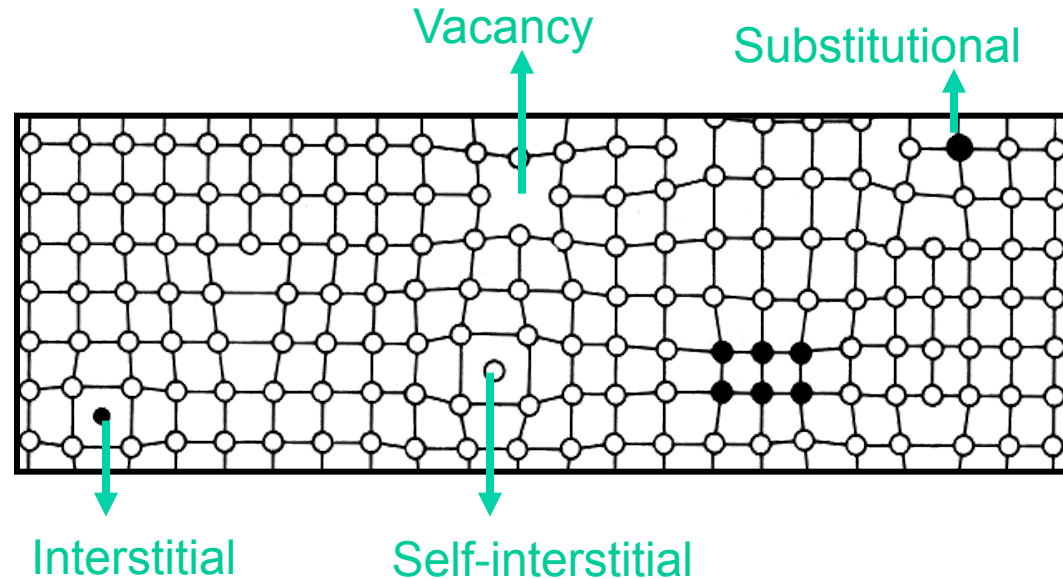
- occupies normal lattice site
- dopant ☺, e.g., P in Si
- contaminant Li^+ in NaCl

2. Interstitial Impurity

- occupies position between lattice sites
- alloying element ☺, e.g., C in Fe
- contaminant, H in Fe

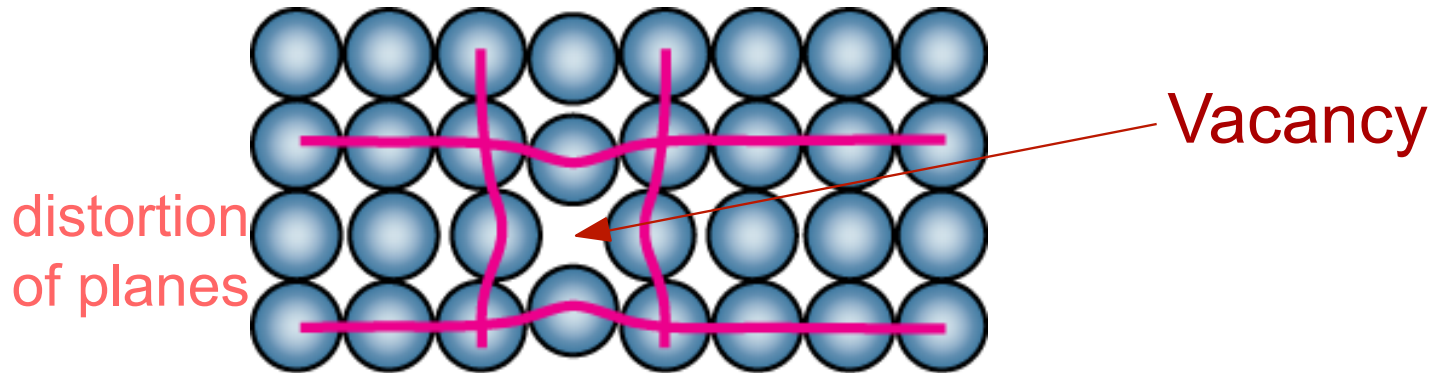
3. Vacancy

- unoccupied lattice site
- formed at time of crystallization

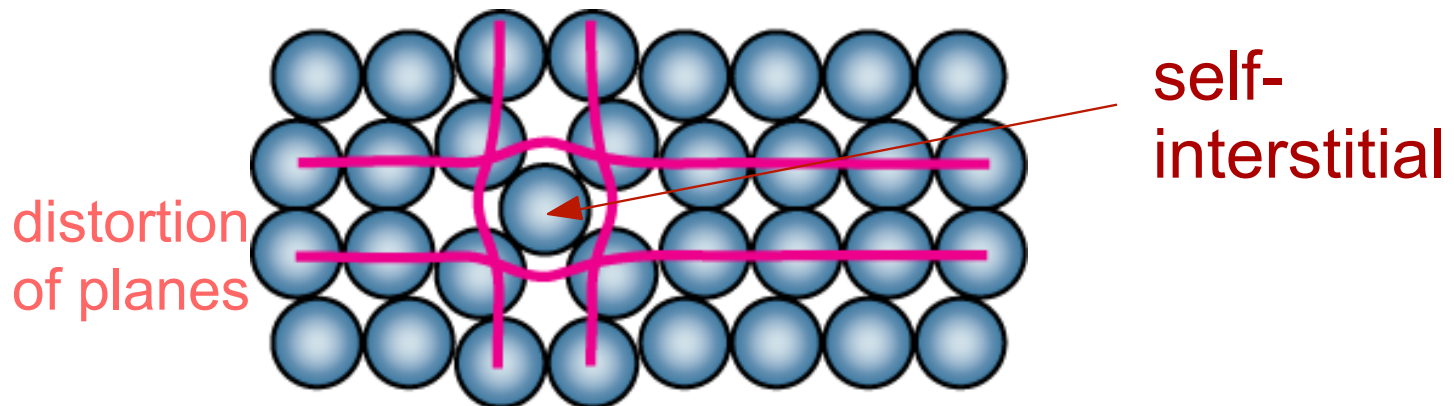


Point Defects

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



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



Equilibrium Concentration: Point Defects

- Equilibrium concentration varies with temperature!

No. of defects $\rightarrow N_v$

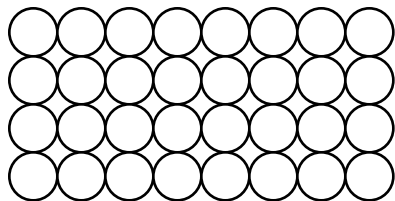
No. of potential defect sites. $\rightarrow N$

Activation energy $\rightarrow Q_v$

Boltzmann's constant $\rightarrow k$

Temperature $\rightarrow T$

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



Each lattice site
is a potential
vacancy site

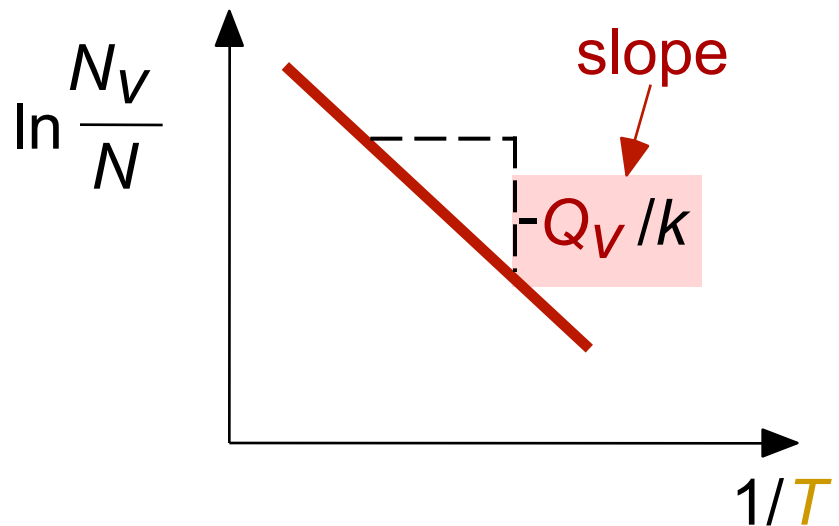
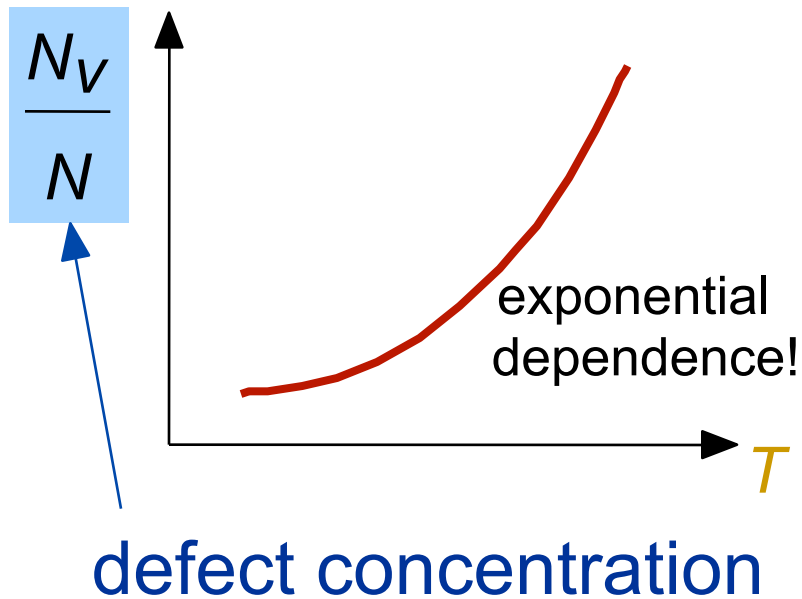
$(1.38 \times 10^{-23} \text{ J/atom-K})$
 $(8.62 \times 10^{-5} \text{ eV/atom-K})$

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 m³ of Cu at 1000°C.
- Given:

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

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

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

Annotations for the equation above:

- Q_v is labeled 0.9 eV/atom (red arrow)
- kT is labeled 1273K (yellow arrow)
- k is labeled $8.62 \times 10^{-5} \text{ eV/atom-K}$ (green arrow)

For 1 m³, $N = \rho \times \frac{N_A}{A_{\text{Cu}}} \times 1 \text{ m}^3 = 8.0 \times 10^{28} \text{ sites}$

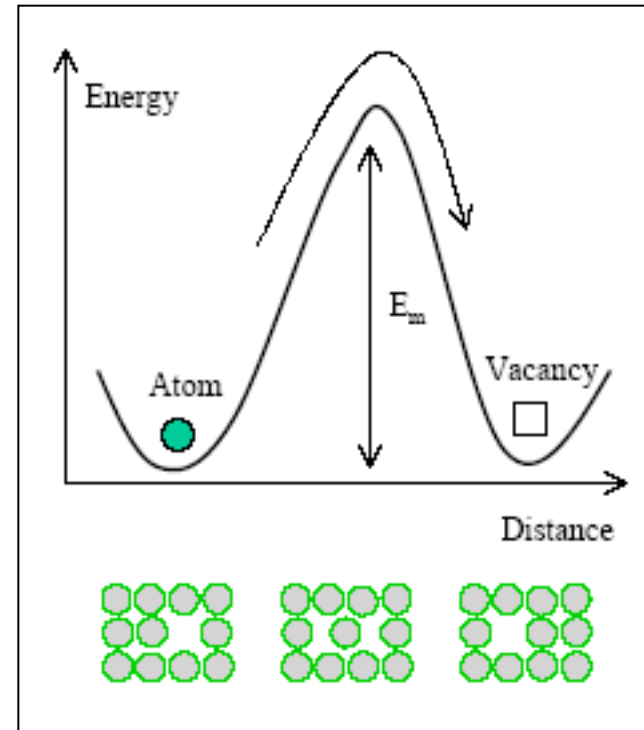
- Answer:

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



Point Defects: Vacancies & Interstitials

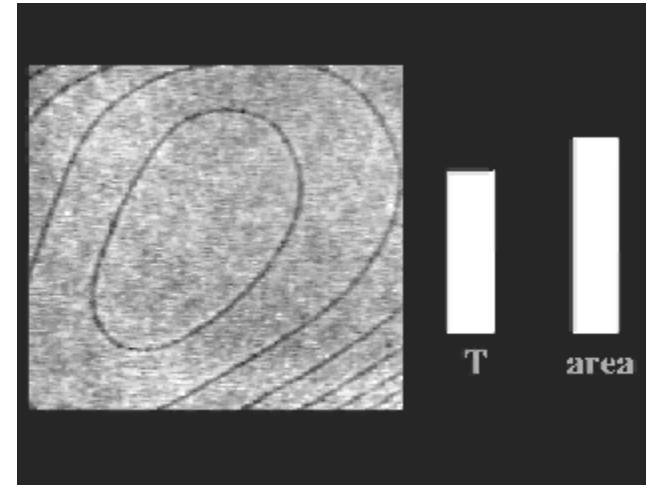
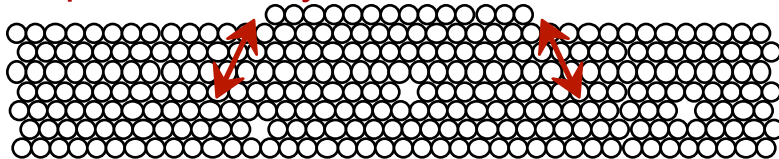
- Most common defects in crystalline solids are point defects.
- At high temperatures, atoms frequently and randomly change their positions leaving behind empty lattice sites.
- In general, **diffusion** (mass transport by atomic motion) - can only occur because of vacancies.



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.

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



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 $5.75\text{ }\mu\text{m}$ by $5.75\text{ }\mu\text{m}$.) Copyright (2001) Macmillan Publishers, Ltd.

Metallic Solid Solutions

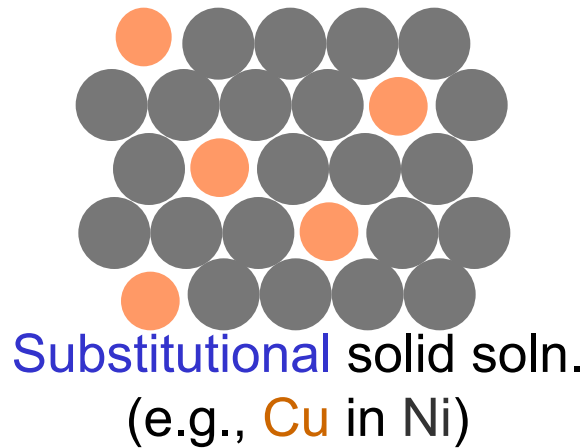
- Most engineering metals are combined with other metals or non-metals to provide increased strength, higher corrosion resistance or other desired properties → «METAL ALLOY»
- Simplest type of alloy = Solid Solution:
A solid that consists of two or more elements atomically dispersed in a **single-phase** structure.



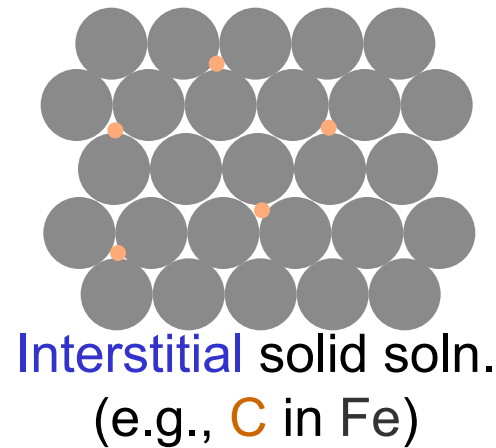
Point Defects in Alloys

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

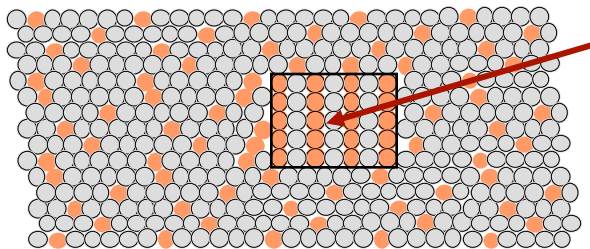
- **Solid solution** of **B** in A (i.e., random dist. of point defects)



OR



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



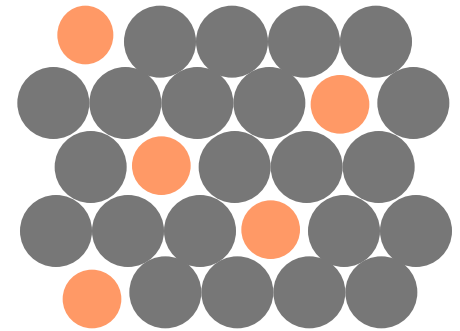
Second phase particle
--different **composition**
--often different structure.

Imperfections in Solids

Conditions for substitutional solid solution (S.S.)

- W. Hume – Rothery rule

- 1. Δr (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



Imperfections in Solids

Application of Hume–Rothery rules – Solid Solutions

Copper and nickel are completely soluble in one another at all proportions.

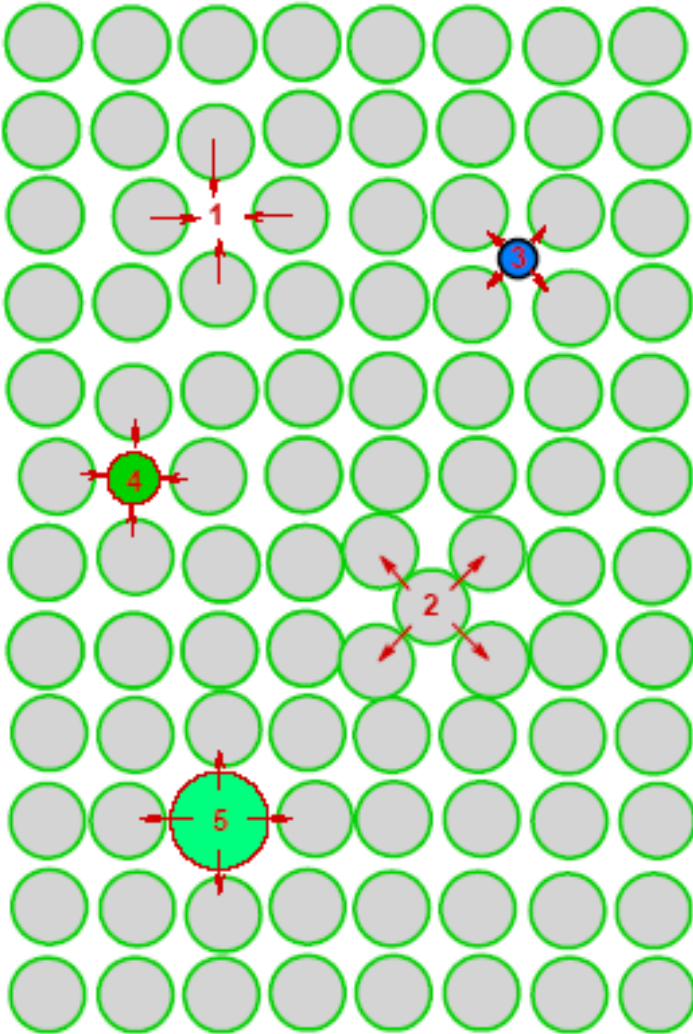
- Atomic radii are closed to each other
- Both have FCC crystal structure
- Electronegativities are comparable
- Valences are +1 (sometimes +2) for Cu and +2 for Ni.

<i>Element</i>	<i>Atomic Radius (nm)</i>	<i>Crystal Structure</i>	<i>Electro-negativity</i>	<i>Valence</i>
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

Table on p. 106, Callister 7e.



Exercise on Point Defects



Schematic representation of a variety of point defects:

ANSWER

The arrows represent the local stresses introduced by the point defects.

Imperfections in Solids

- Specification of composition

- weight percent $C_1 = \frac{m_1}{m_1 + m_2} \times 100$

m_1 = mass of component 1

- atom percent $C'_1 = \frac{n_{m1}}{n_{m1} + n_{m2}} \times 100$

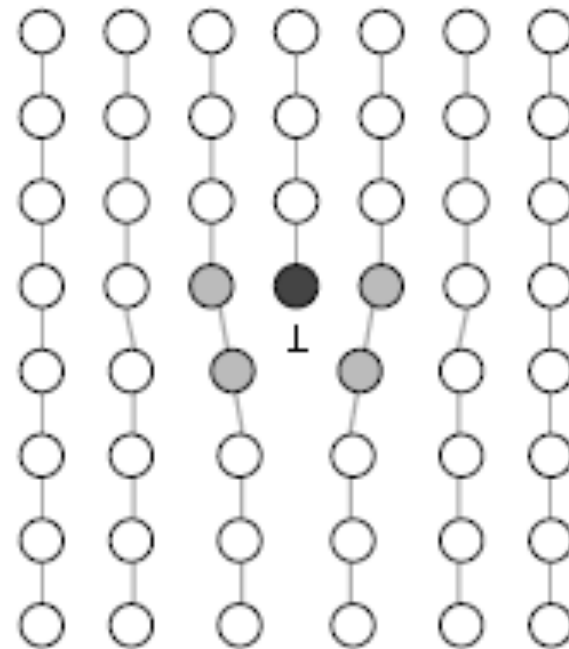
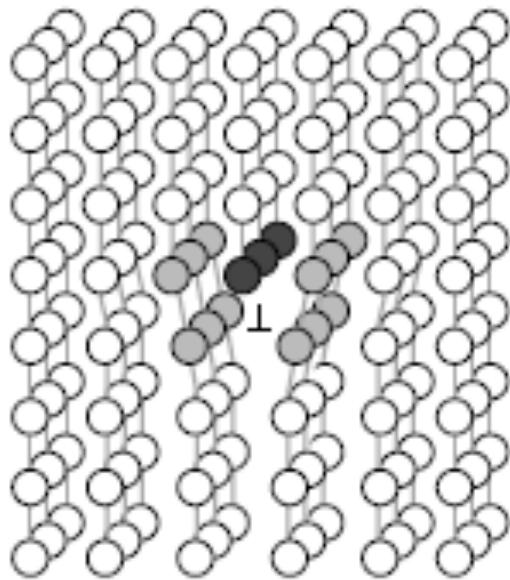
n_{m1} = number of moles of component 1



1 Dimensional Line Defects

Dislocations

- **Dislocations are linear defects:** the interatomic bonds are distorted only in the vicinity of the dislocation line. This area is called the **dislocation core**.
- Dislocations also create small elastic deformations of the lattice at large distances.



Imperfections in Solids

Linear Defects (Dislocations)

- Are one-dimensional defects around which atoms are misaligned
- Edge dislocation:
 - extra half-plane of atoms inserted in a crystal structure
 - $\mathbf{b} \perp$ to dislocation line
- Screw dislocation:
 - spiral planar ramp resulting from shear deformation
 - $\mathbf{b} \parallel$ to dislocation line

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



Imperfections in Solids

Edge Dislocation

Extra half-plane of atoms inserted in a crystal structure
 $\mathbf{b} \perp$ to dislocation line

- Centers on the line that is defined along the end of the extra half-plane of the atoms. dislocation line
- Above dis. line. Atoms are squeezed together, below are pulled apart.
- Magnitude of distortion decreases with distance away from the dislocation line.

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

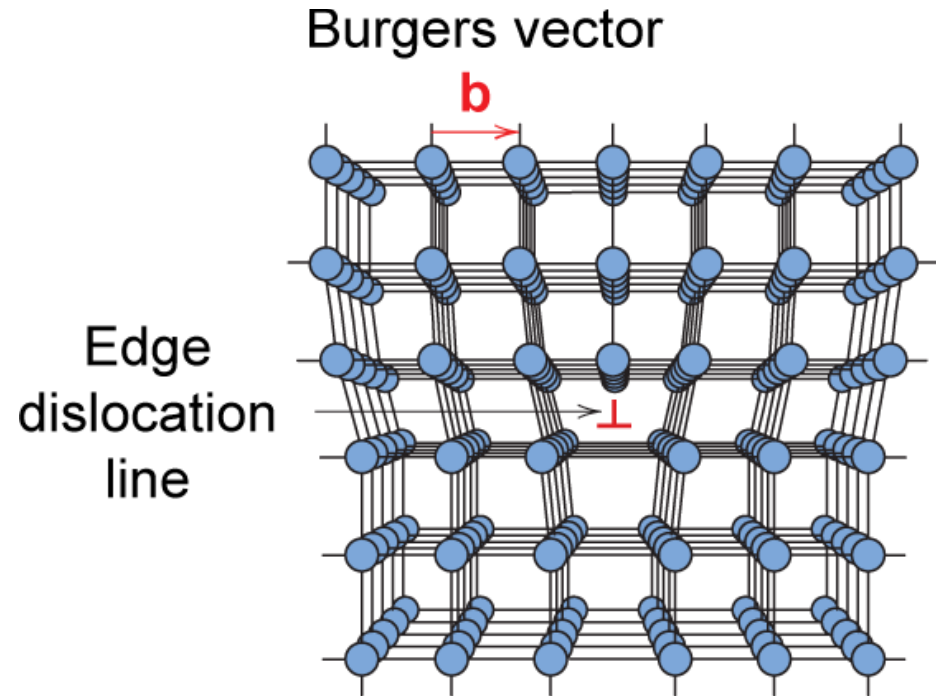
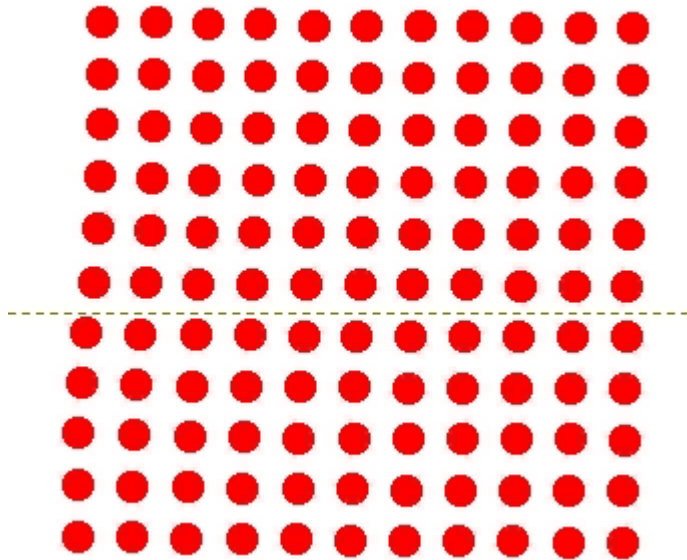


Fig. 4.3, Callister 7e.

Motion of Edge Dislocation

- 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.

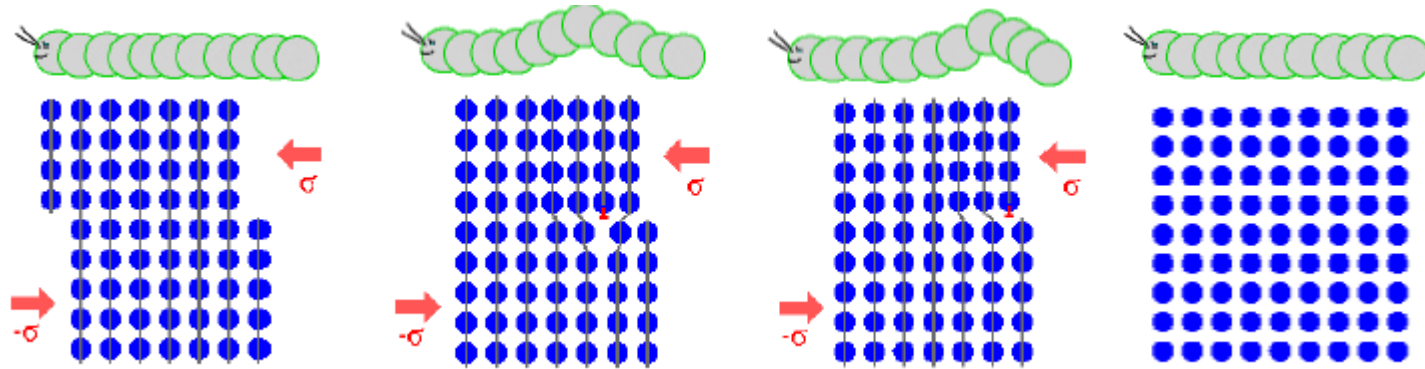


Atomic view of edge dislocation motion from left to right as a crystal is sheared.

(Courtesy P.M. Anderson)



DISLOCATIONS



- Material *permanently* deforms as dislocation moves through the crystal.
- Bonds break and reform, but *only along the dislocation line* at any point in time, not along the whole plane at once.
- *Dislocation line* separates slipped and unslipped material.

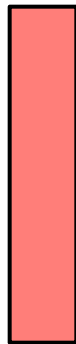
Line Defects

Dislocations:

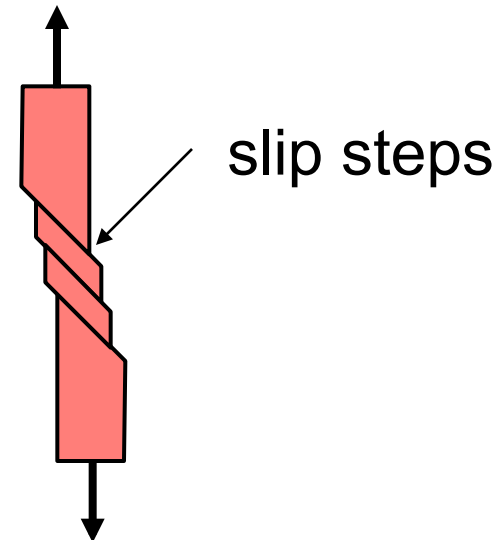
- are line defects,
- slip between crystal planes result when dislocations move,
- produce permanent (plastic) deformation.

Schematic of Zinc (HCP):

- before deformation



- after tensile elongation



Adapted from Fig. 7.8, *Callister 7e*.

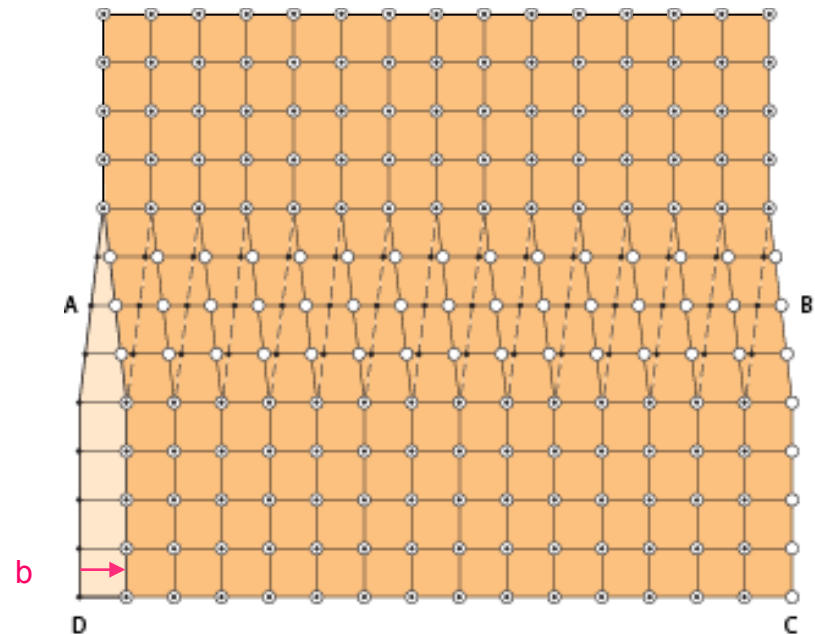
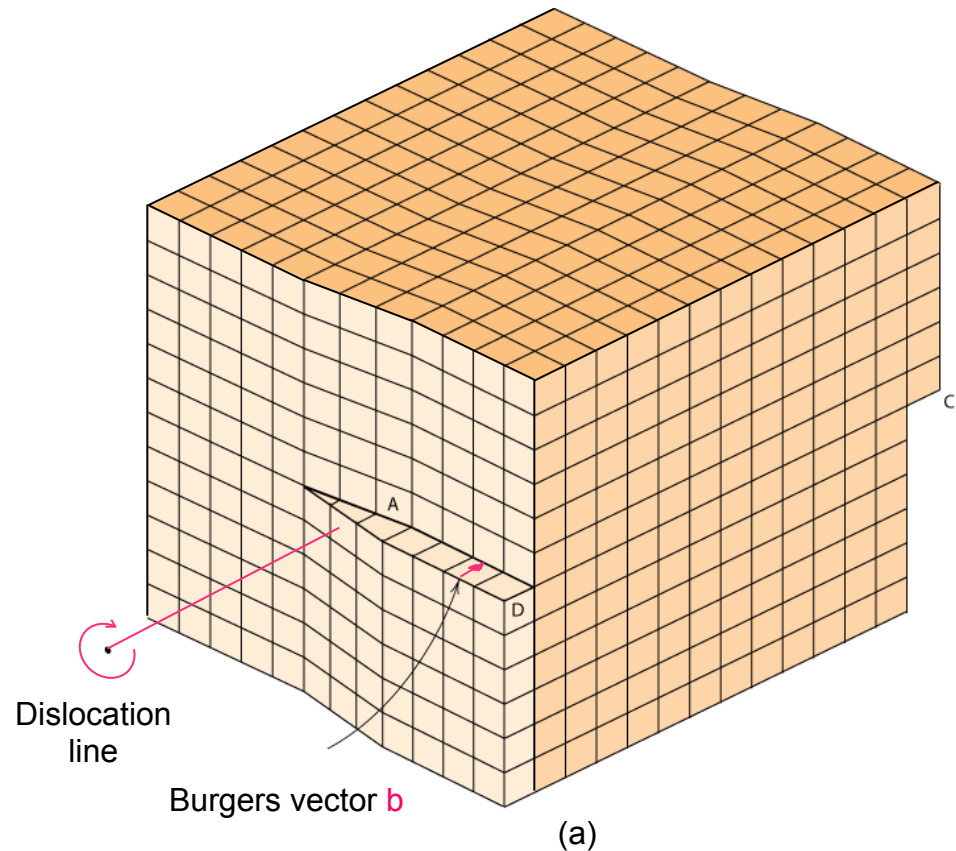
Imperfections in Solids

Screw Dislocation:

Spiral planar ramp resulting from shear deformation

$\mathbf{b} \parallel$ to dislocation line

The upper front region of the crystal is shifted one atomic distance to the right relative to the bottom portion.



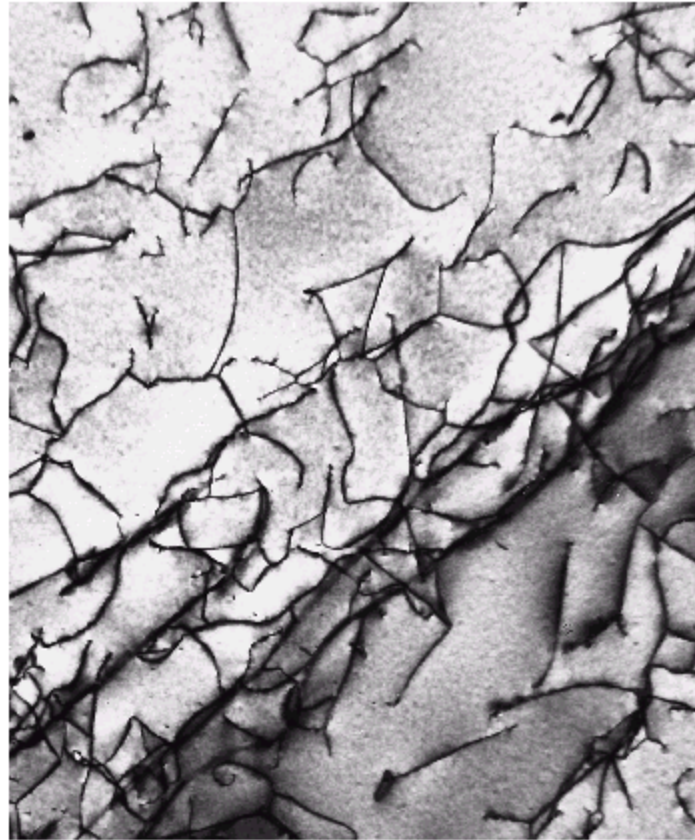
(b) As viewed from above

Adapted from Fig. 4.4, *Callister 7e*.



Imperfections in Solids

Dislocations are visible in electron micrographs



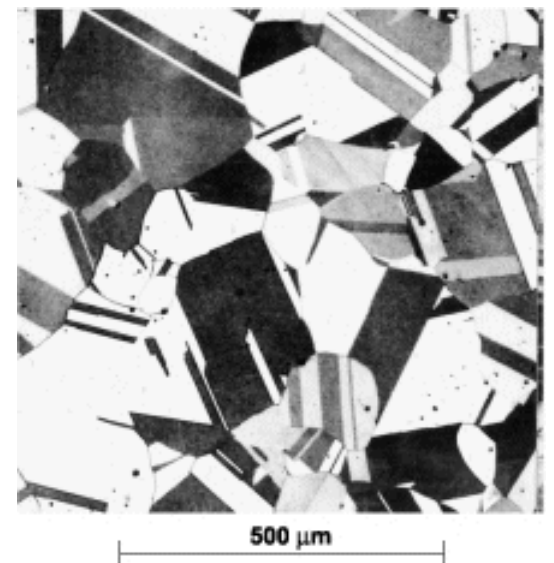
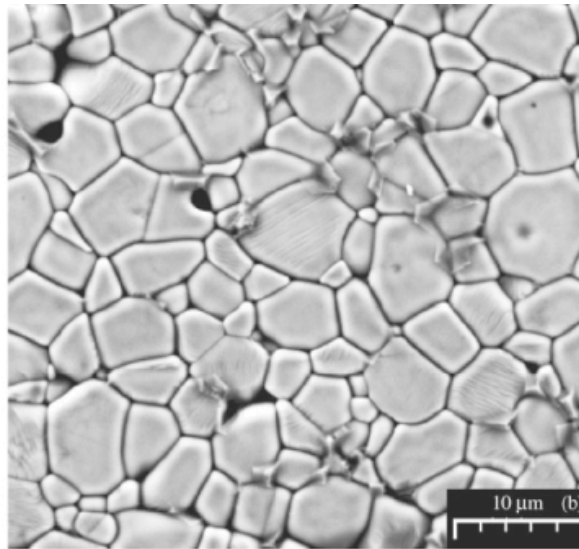
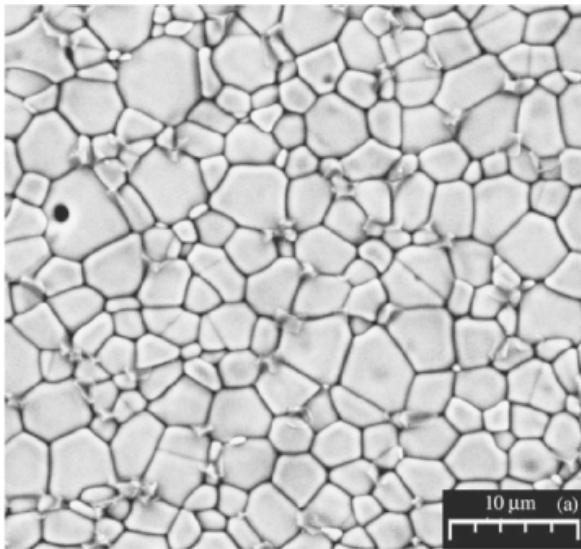
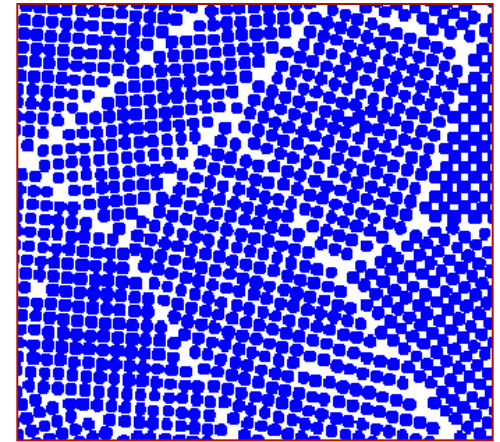
Adapted from Fig. 4.6, *Callister 7e*.



2 Dim. Interfacial Defects or Boundaries

Grain Boundaries:

Surface imperfections in polycrystalline materials that separate grains (crystals) of different orientation.



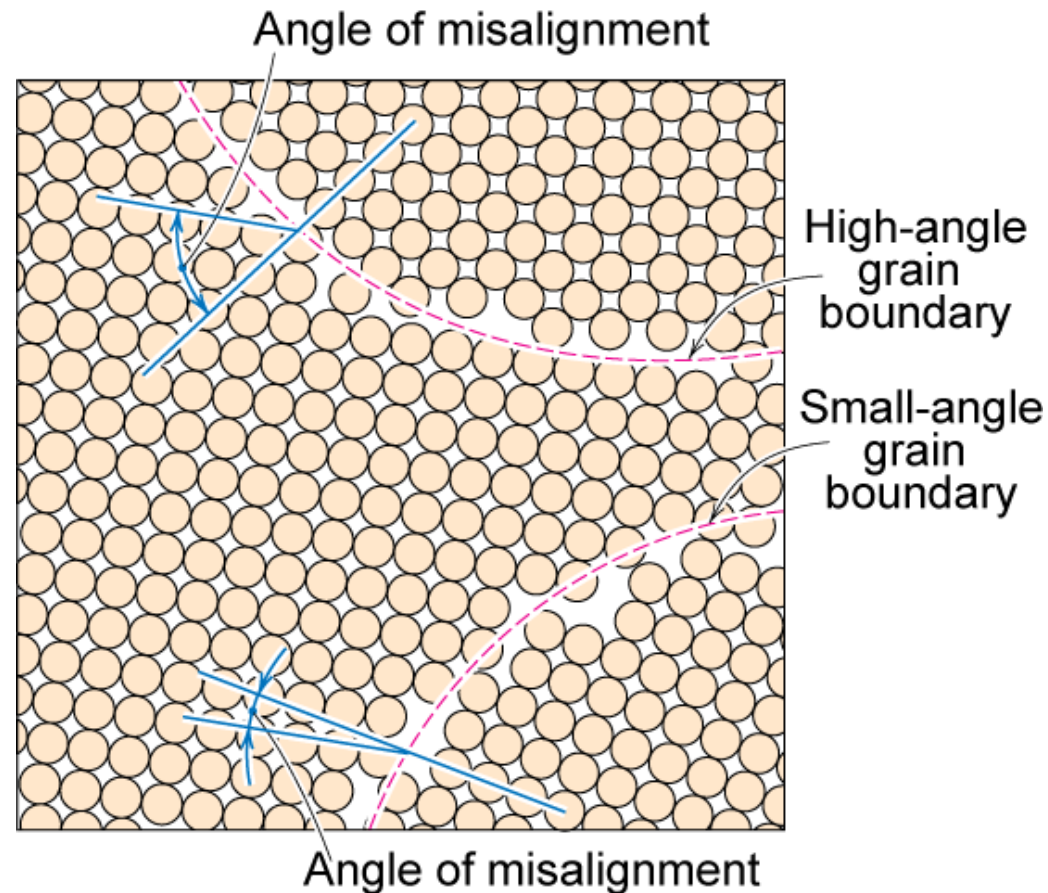
SEM (Scanning electron microscope) image
(showing grains and grain boundaries)

*Photomicrographs of typical
microstructures of annealed
brass*

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

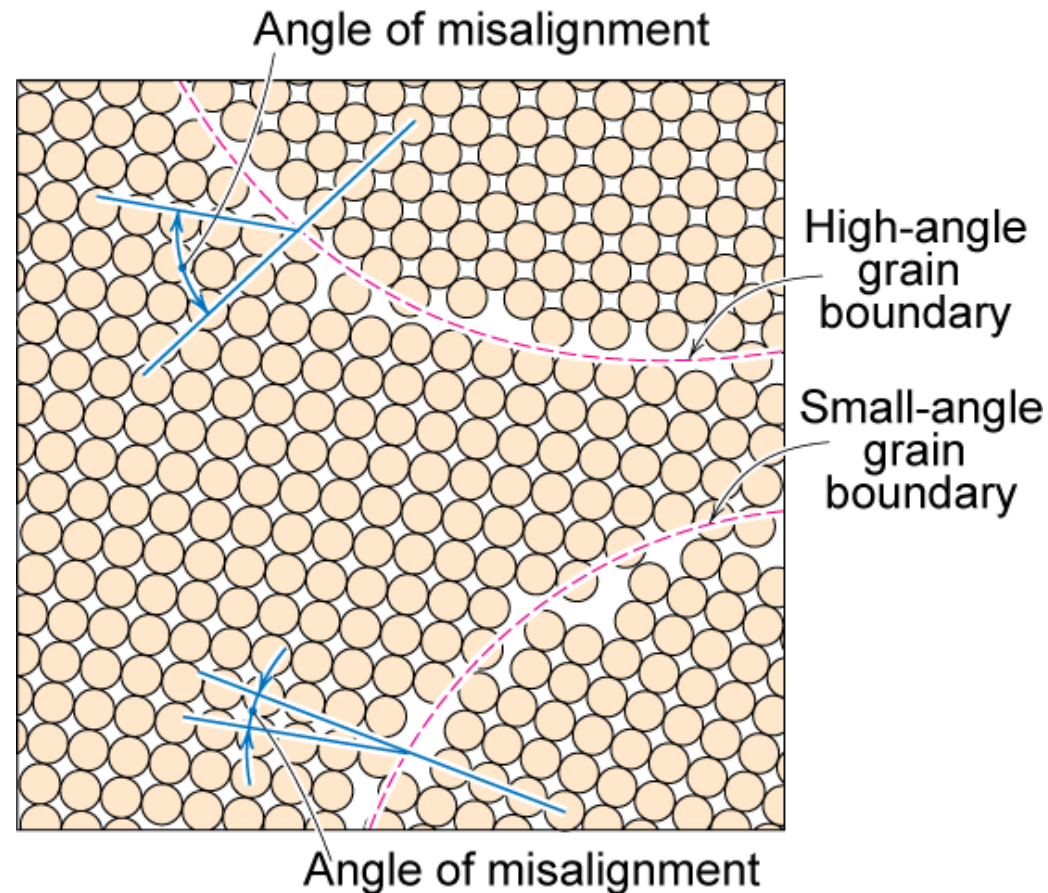


Adapted from Fig. 4.7, *Callister 7e*.

Polycrystalline Materials

Grain Boundaries

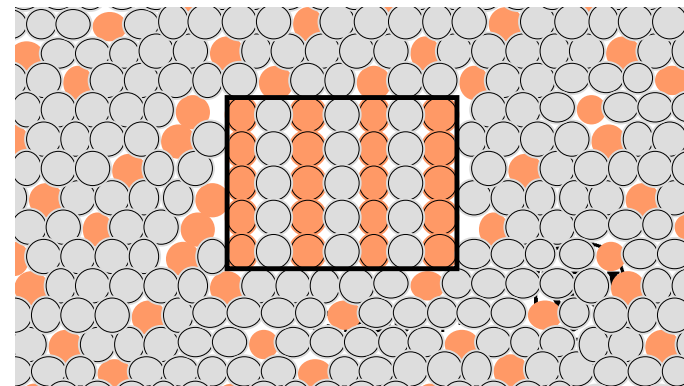
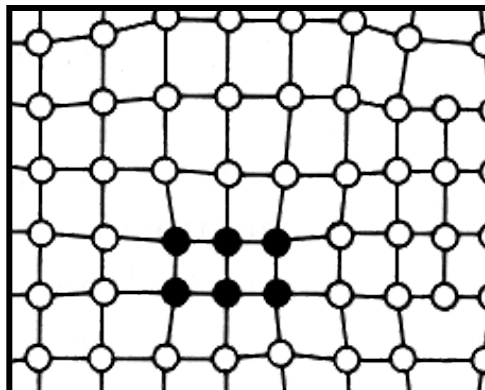
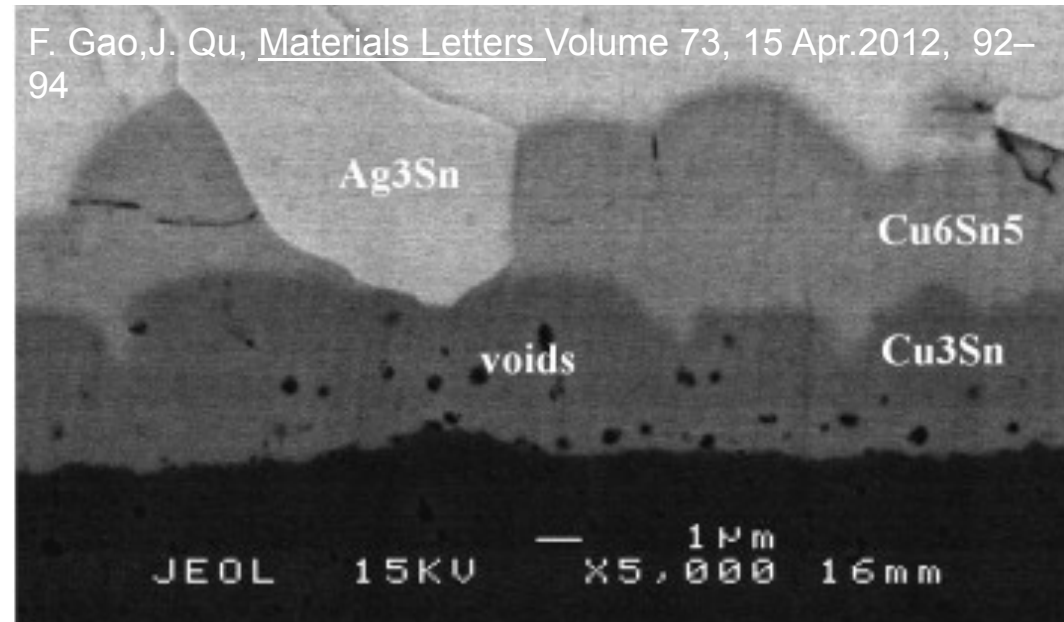
- Transition from lattice of one region to that of the other (there is some atomic mismatch)
- The angle of misalignment btw grains is large for high angle grain boundary
- Small- (or low-) angle grain boundary: orientation mismatch is slight



Adapted from Fig. 4.7, *Callister 7e*.

3 Dim: Volume Defects

- Form when a cluster of point defects join
- Vacancies join:
 - **voids**
 - **Pores**
- **Cracks**
- Cluster of impurity atoms join
→ **precipitate**



Experimental Techniques for Identification of Microstructure and Defects



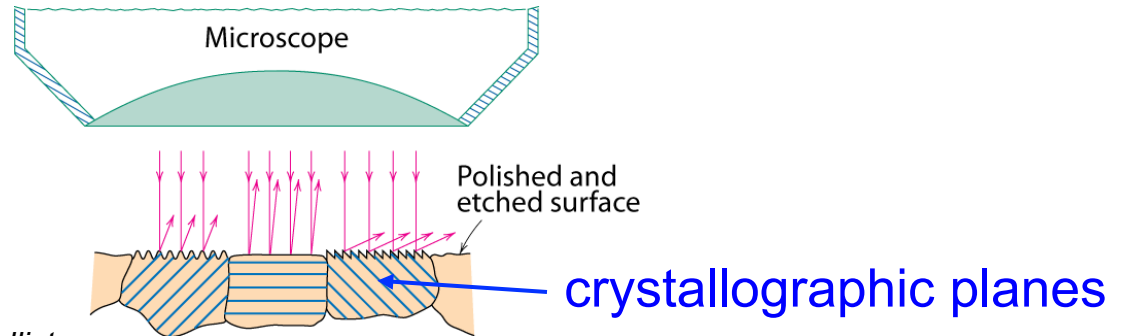
Microscopic Examination

- Crystallites (grains) and grain boundaries.
Vary considerably in size. Can be quite large
 - ex: Large single crystal of quartz or diamond or Si
 - ex: Aluminum light post or garbage can - see the individual grains
- Crystallites (grains) can be quite small (mm or less) – necessary 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.



Adapted from Fig. 4.13(b) and (c), *Callister 7e*. (Fig. 4.13(c) is courtesy of J.E. Burke, General Electric Co.



Micrograph of brass (a Cu-Zn alloy)

← 0.75mm →

Microscopy

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

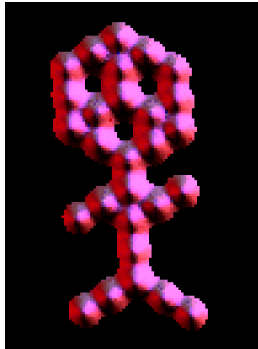
For higher resolution need higher frequency

- 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.

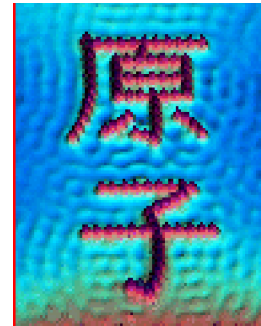


Scanning Tunneling Microscopy (STM)

- Atoms can be arranged and imaged!



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

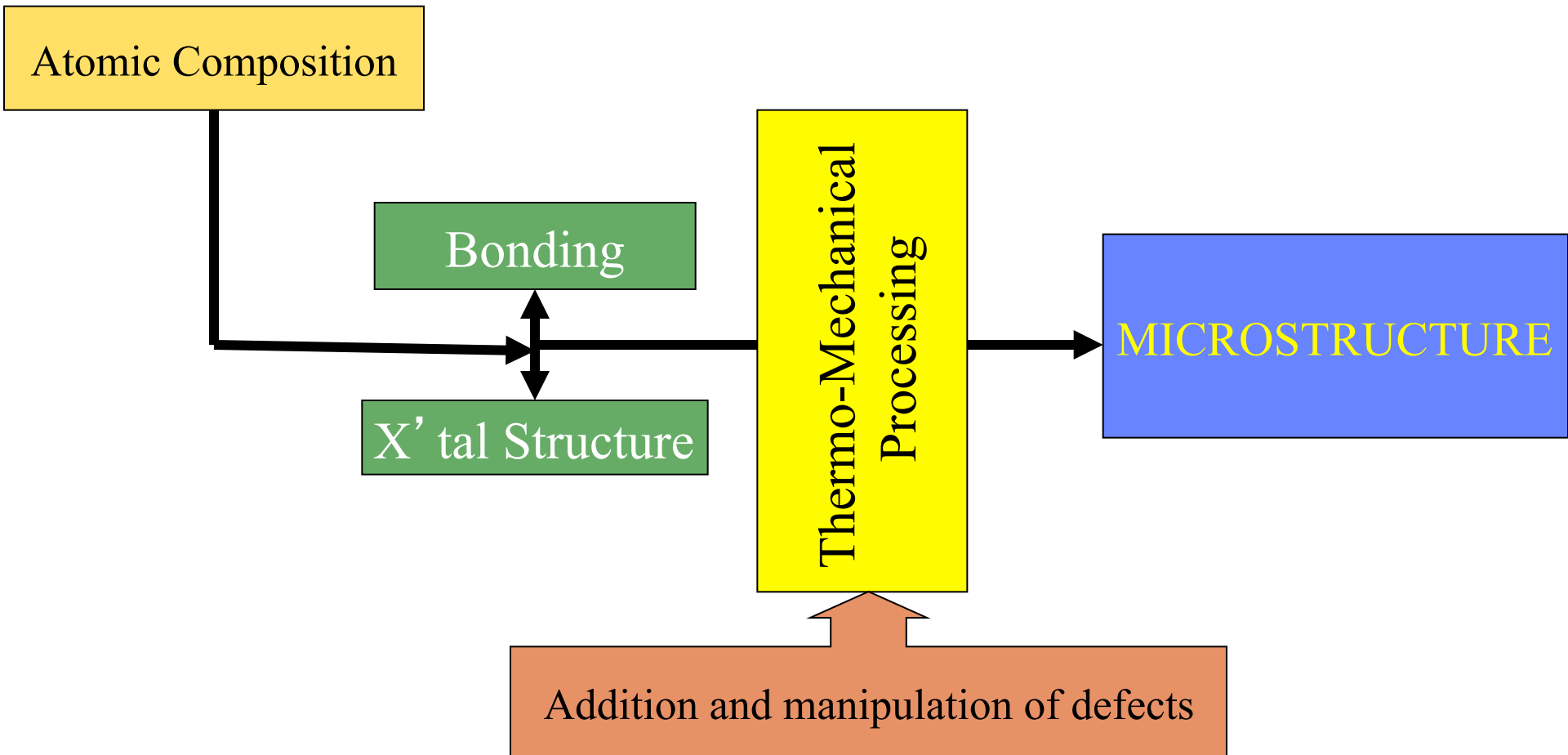


Iron atoms arranged on a copper (111) surface. These Kanji characters represent the word “atom”.

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



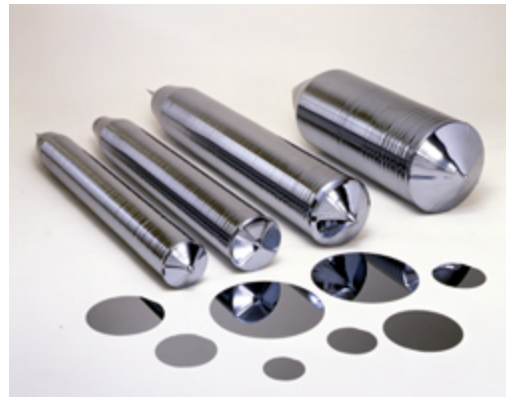
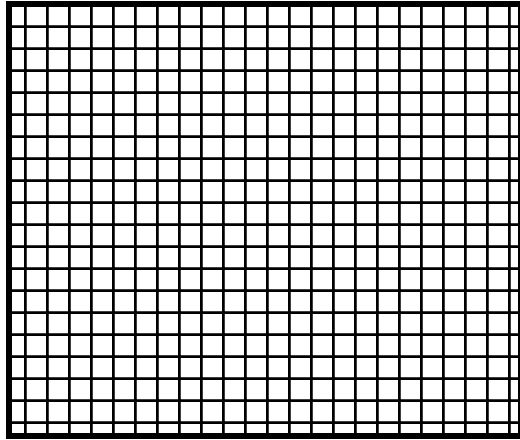
SUMMARY



Disorder

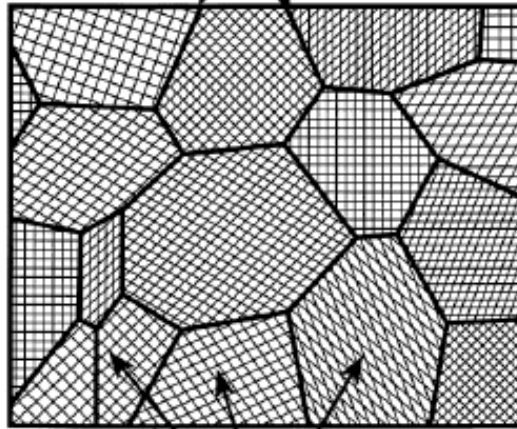


Single Crystal

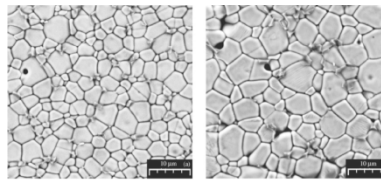
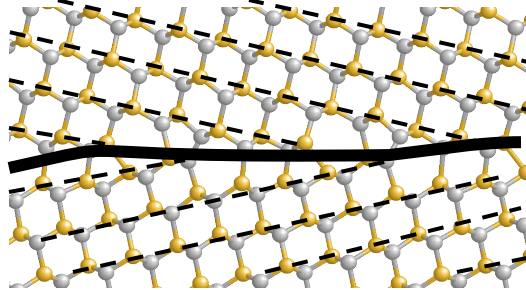


Polycrystalline

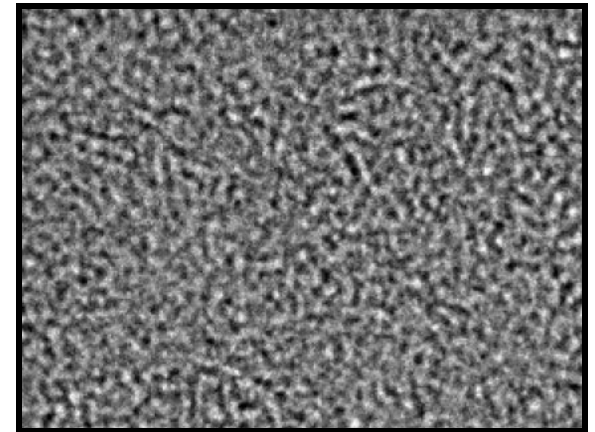
Grain boundaries



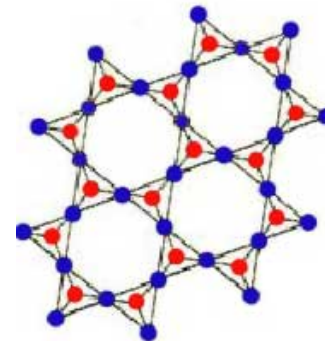
Grains



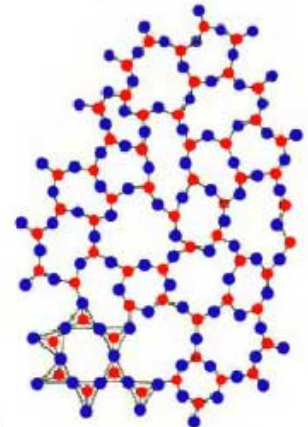
Amorphous



Crystalline SiO_2
(Quartz)



Amorphous SiO_2
(Glass)



• Si • O

Summary

- Point, Line, and Area defects exist 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.)

