Physics of Materials: Imperfection

Dr. Anurag Srivastava

Atal Bihari Vajpayee

Indian Institute of Information Technology and Management, Gwalior

Imperfections in Solids

"Crystals are like people, it is the defects in them which tend to make them interesting!"

Prof. Colin Humphreys

Properties of Materials affected by defects

Mechanical: Dislocation

Electronic:

Conduction in electronic ceramic (vacancies)

Mobility in semiconductors

Diffusions: Vacancies and Interstitials

Optical: recombination centers

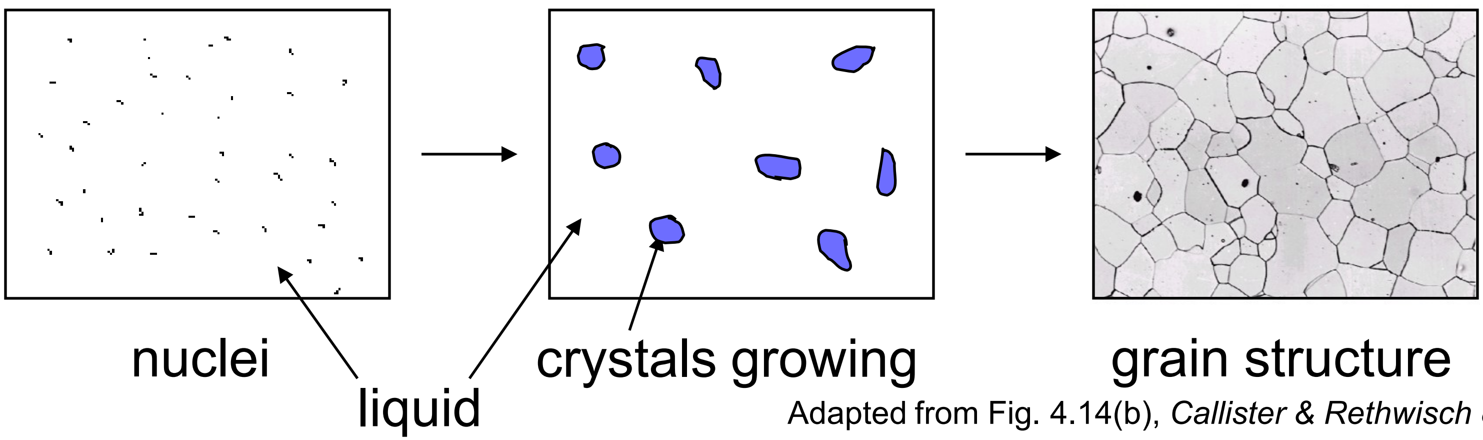
Imperfections in Solids

Possible Learning

- The solidification mechanisms
- Types of defects arise in solids
- Can the number and type of defects be varied and controlled?
- How do defects affect material properties?
- Are the 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



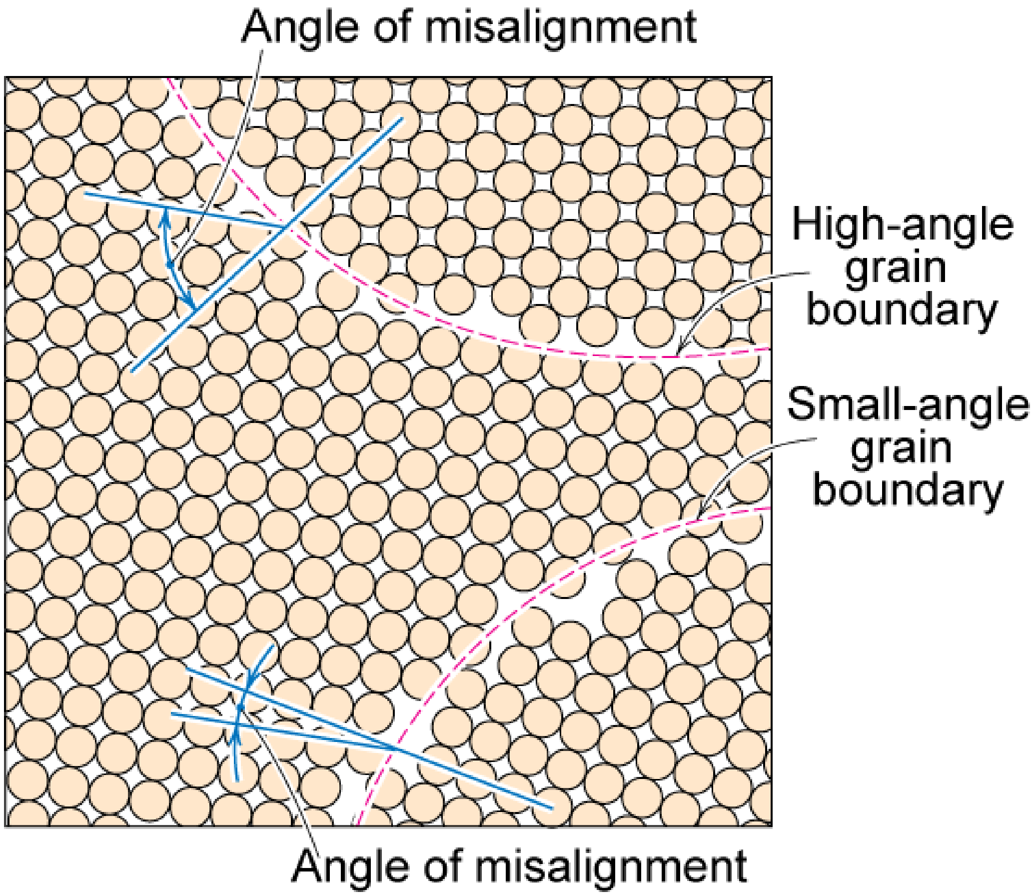
Adapted from Fig. 4.14(b), *Callister & Rethwisch 8e.*

- Crystals grow until they meet each other

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

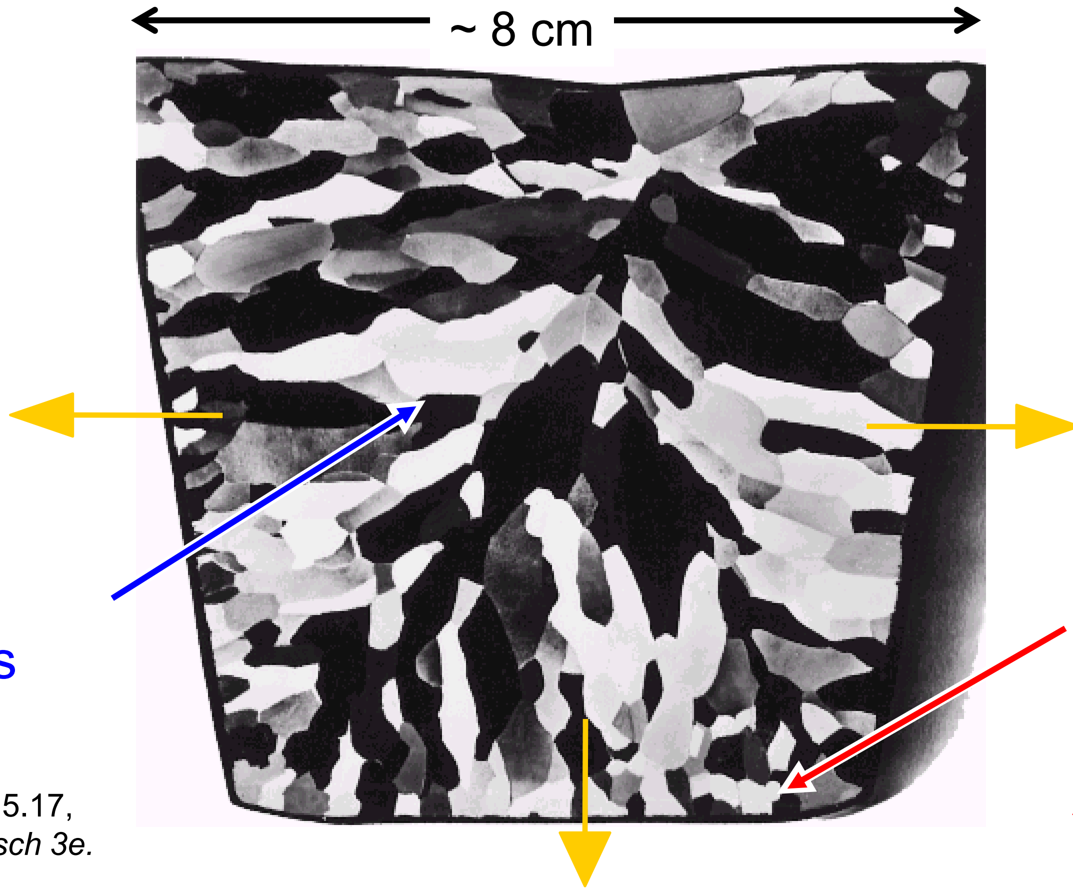


Adapted from Fig. 4.7, *Callister & Rethwisch 8e.*

Solidification

Grains can be - equiaxed (roughly same size in all directions)

- columnar (elongated grains)



Adapted from Fig. 5.17,
Callister & Rethwisch 3e.

Grain Refiner - added to make smaller, more uniform, equiaxed grains.

Imperfections in Solids

There is no such thing as a perfect crystal.

- What are these imperfections?
- Why are they important?

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

Types of Imperfections

- Vacancy atoms
- Interstitial atoms
- Substitutional atoms

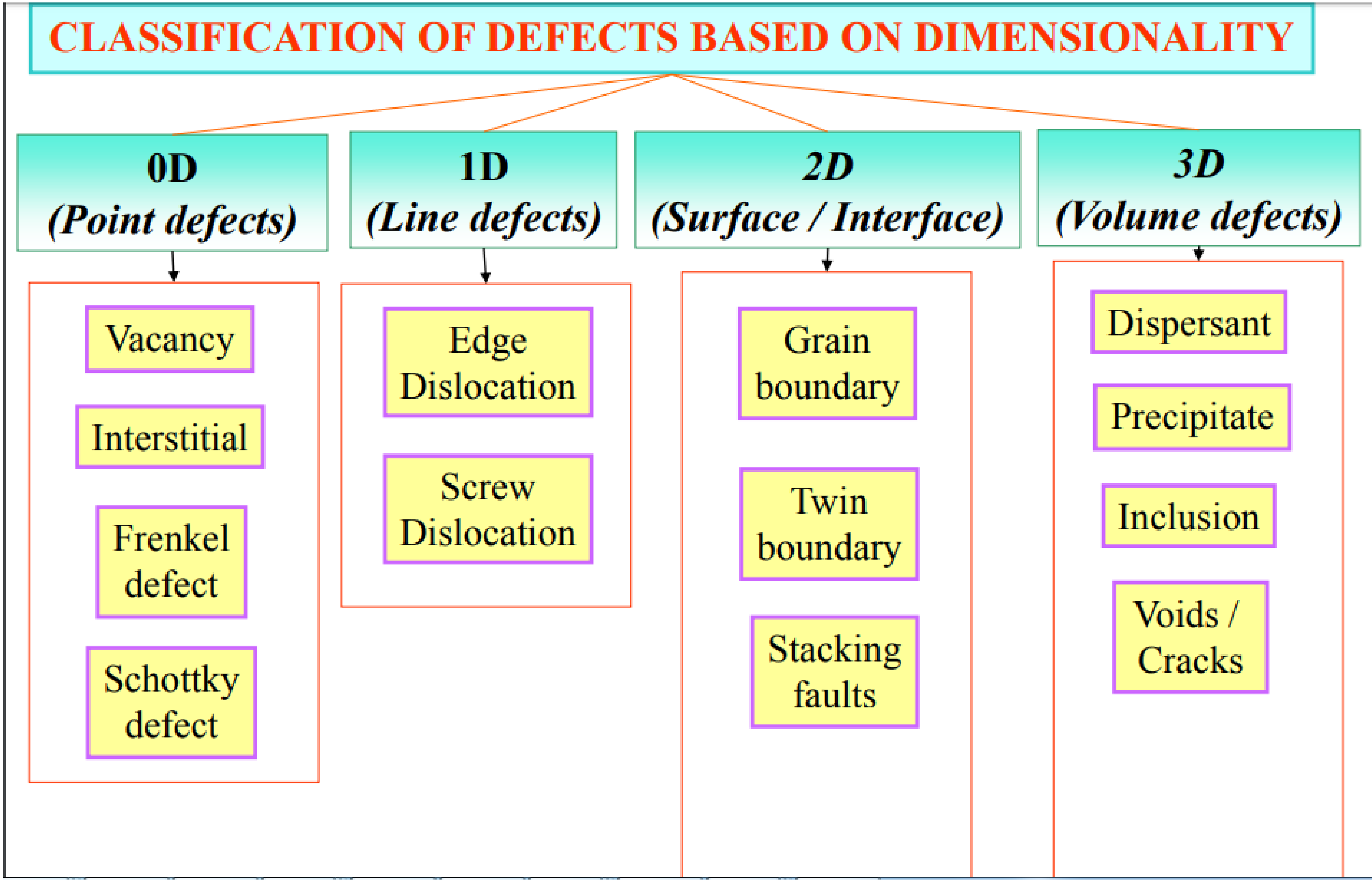
Point defects

- Dislocations

Line defects

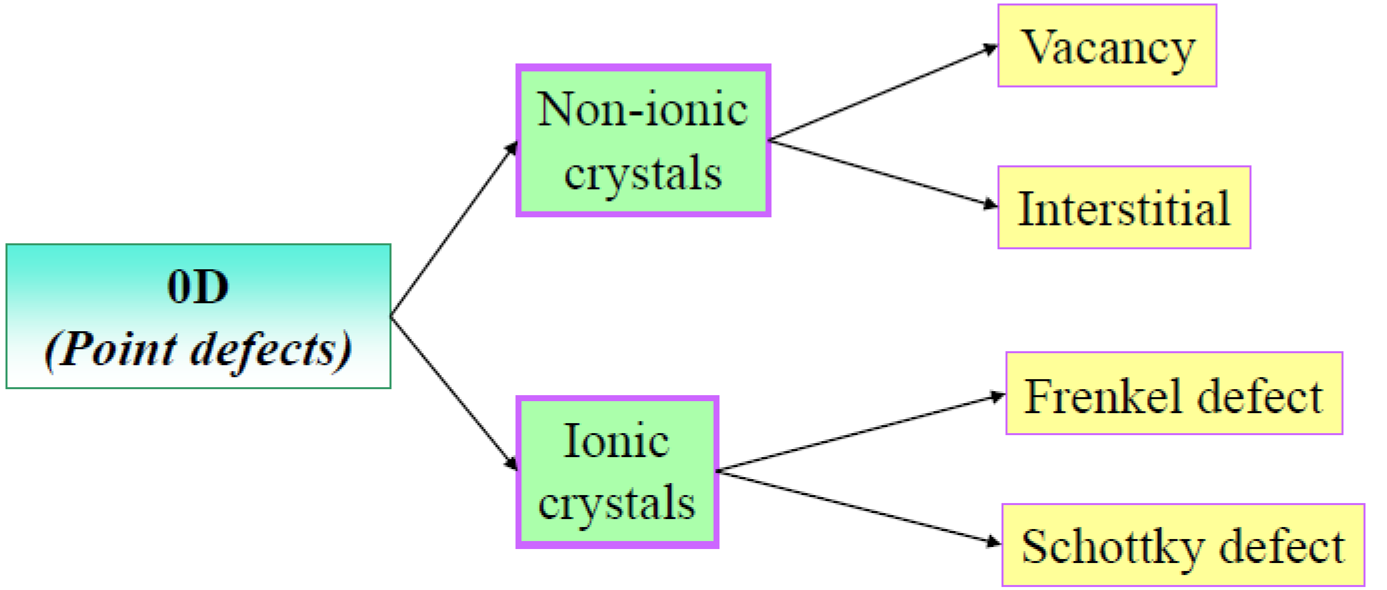
- Grain Boundaries

Area defects


CLASSIFICATION OF DEFECTS BASED ON DIMENSIONALITY
0D
(Point defects)
1D
(Line defects)
2D
(Surface / Interface)
3D
(Volume defects)
Vacancy
Interstitial
Frenkel defect
Schottky defect
Edge Dislocation
Screw Dislocation
Grain boundary
Twin boundary
Stacking faults
Dispersant
Precipitate
Inclusion
Voids / Cracks

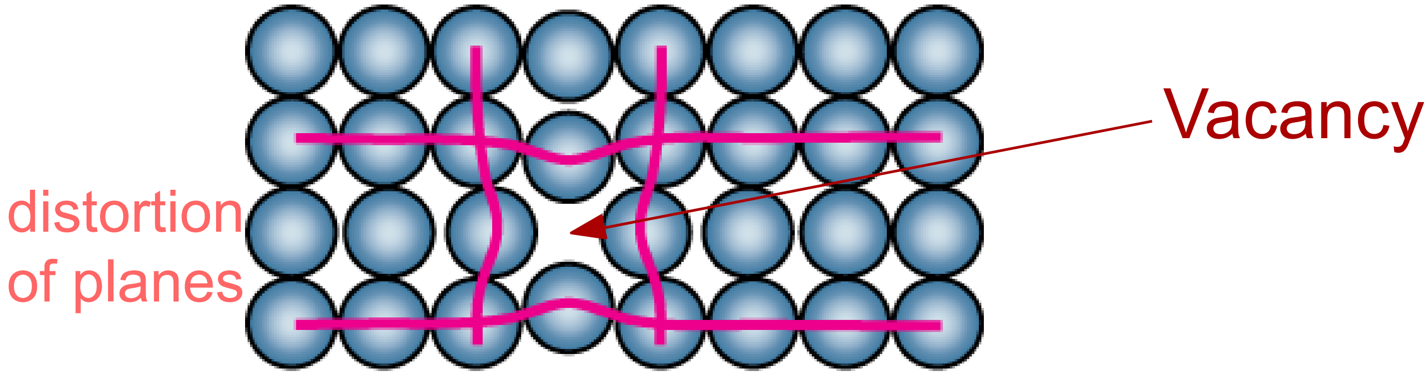
POINT DEFECTS

Point Defects are the irregularities or deviations from ideal arrangement around a point or an atom in a crystalline substance.

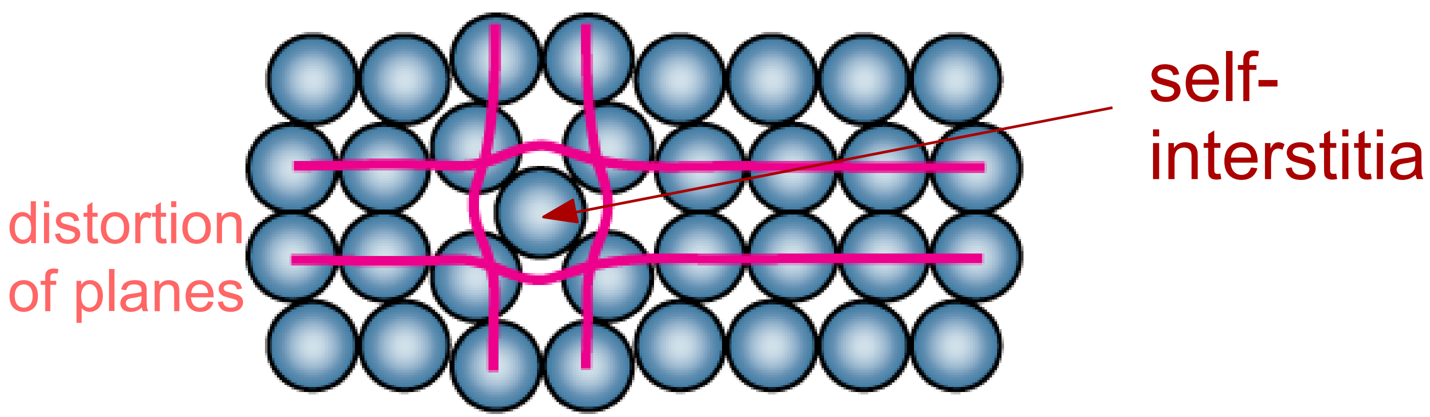


Point Defects in Metals

- 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

Activation energy

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

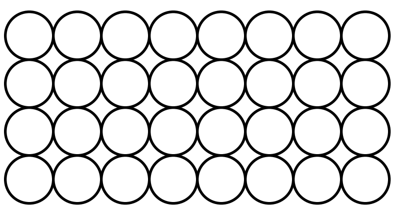
No. of potential defect sites

Temperature

Boltzmann's constant

(1.38×10^{-23} J/atom-K)

(8.62×10^{-5} eV/atom-K)



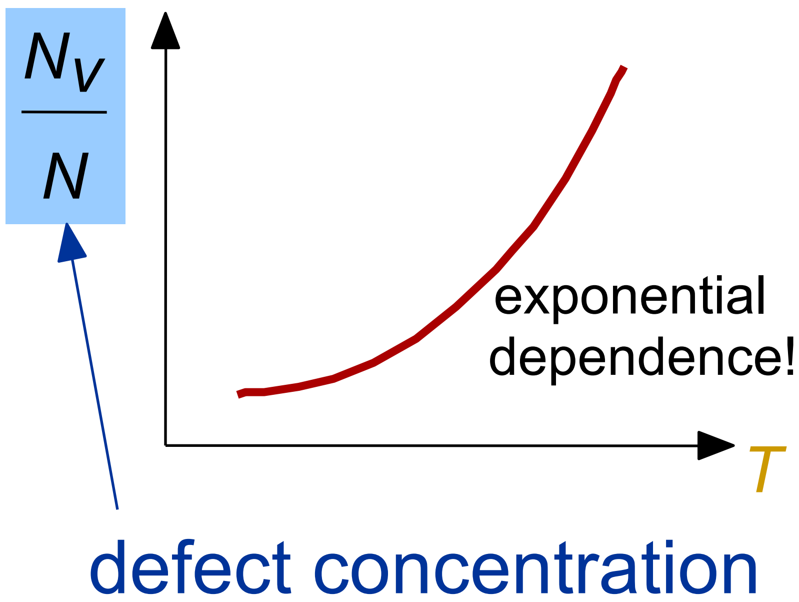
Each lattice site is a potential vacancy site

Measuring Activation Energy

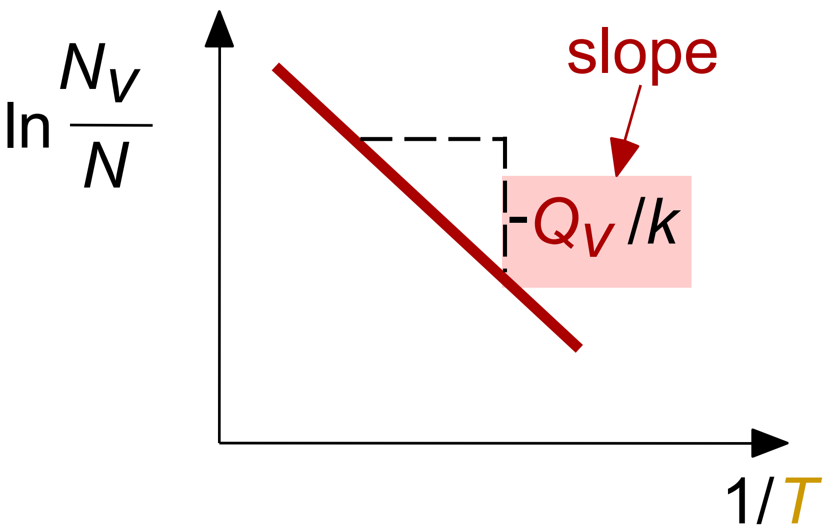
- We can get Q_v from an experiment.

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

- Measure this...



- Replot it...



VACANCY DEFECT

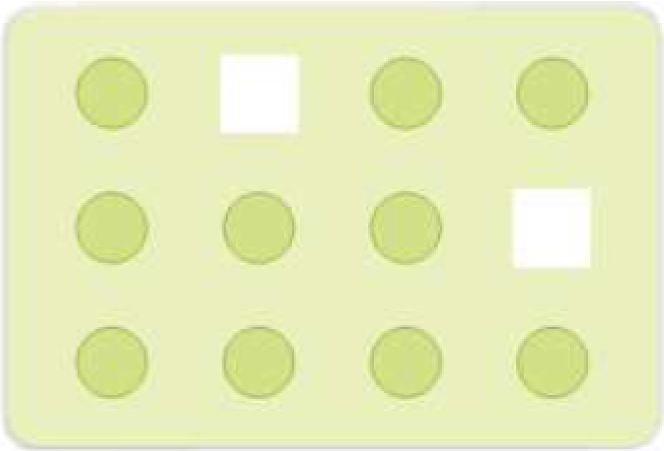
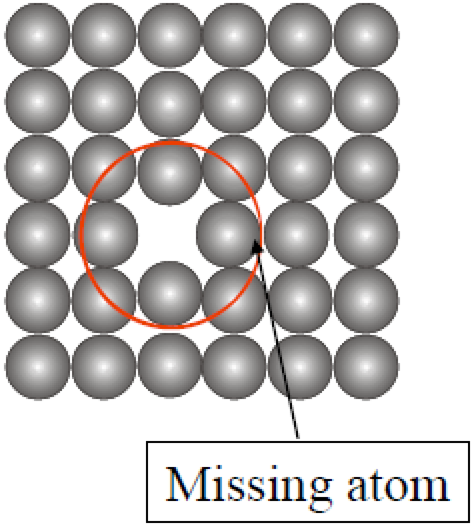


Fig. 1.23: Vacancy defects



- Atom missing from an atomic site
- Occur due to imperfect packing during crystallisation
- This results in decrease in density of the substance
- Number of vacancy defects depend on temperature

Estimating Vacancy Concentration

- Find the equil. # of vacancies in 1 m^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/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

$$N = \frac{N_A \rho}{A_{Cu}} = \frac{(6.022 \times 10^{23}\ \text{sites/mol})(8.4\ g/cm^3)}{63.5\ g/mol}\left(\frac{10^6\ cm^3}{m^3}\right)$$

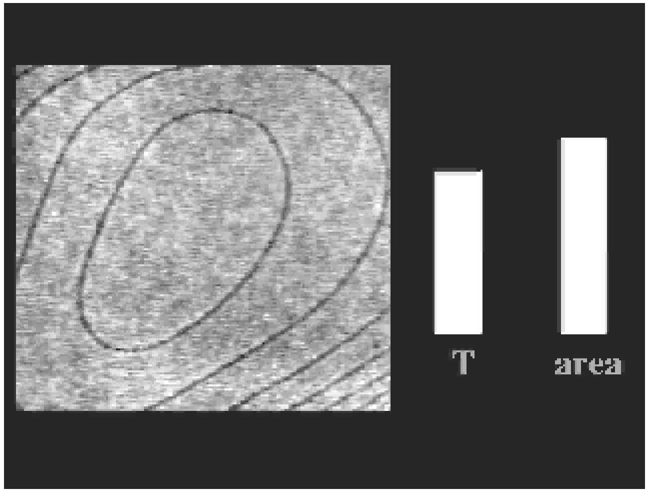
$$N_V = N \exp\left(\frac{-Q_V}{kT}\right) = N \exp\left(\frac{-0.9\ eV/atom}{(8.62 \times 10^{-5}\ eV/atom\text{-}K)(1273\ K)}\right)$$

- Answer:

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

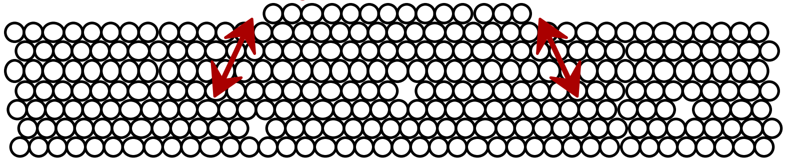
Observing Equilibrium Vacancy Conc.

- Low energy electron microscope view of a (110) surface of NiAl.
- Increasing temperature 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.

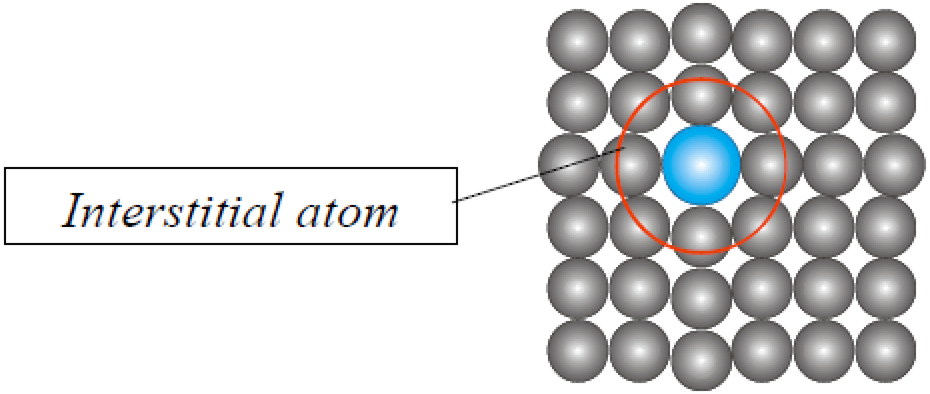


Reprinted with permission from Nature (K.F. McCarty, J.A. Nobel, and N.C. Bartelt, "Vacancies in Solids and the Stability of Surface Morphology", Nature, Vol. 412, pp. 622-625 (2001). Image is 5.75 μm by 5.75 μm.) Copyright (2001) Macmillan Publishers, Ltd.

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



INTERSTITIALS DEFECT

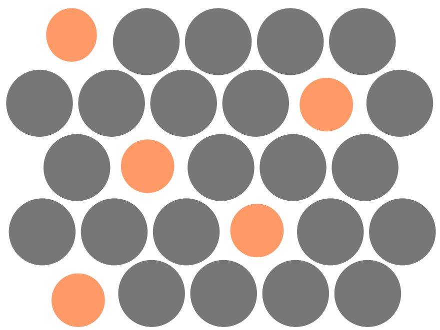


- Addition of an extra atom within a crystal structure
- This defect increases the density of the substance
- Causes atomic distortion
- Vacancy and interstitials are inverse phenomena

Imperfections in Metals (i)

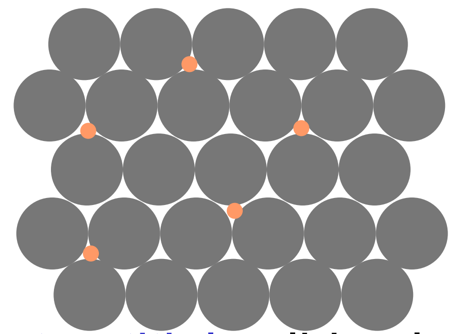
Two outcomes if impurity (B) added to host (A):

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



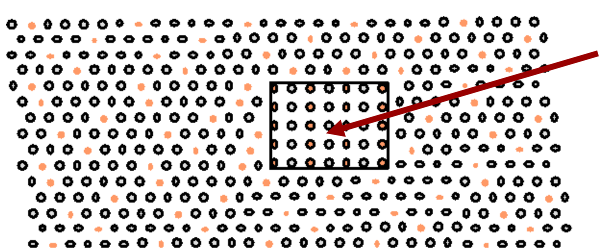
Substitutional solid soln.
(e.g., Cu in Ni)

OR



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.

SCHOTTKY DEFECT

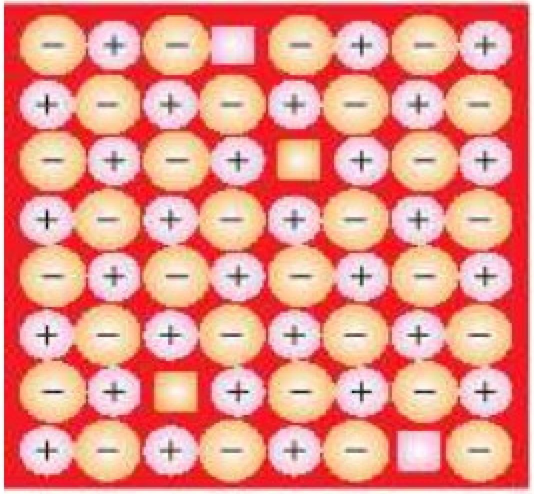
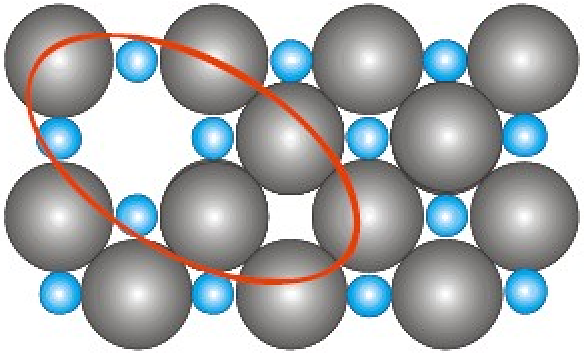


Fig. 1.26: Schottky defects



- Pair of anion and cation vacancies
- In order to maintain electrical neutrality, the number of missing cations and anions are equal
- It also decreases the density of crystal
- E.g. Alkali halides such as NaCl, KF, etc.

FRENKEL DEFECTS

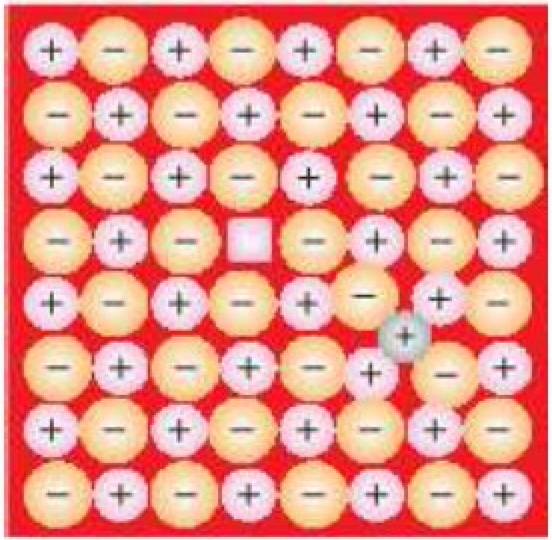
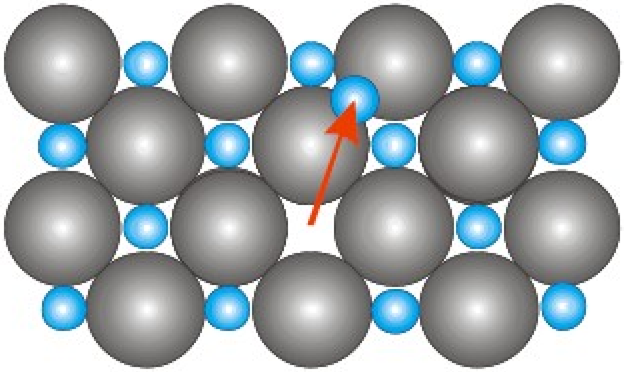


Fig. 1.25: Frenkel defects



- Cation (being smaller get displaced to interstitial voids
- Combination of vacancy and interstitial atom
- No change in the density
- E.g. AgI, CaF_2

Imperfections in Metals (ii)

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 Metals (iii)

Application of Hume–Rothery rules – Solid Solutions

1. Would you predict more Al or Ag to dissolve in Zn?

2. More Zn or Al in Cu?

Element	*Atomic Radius (nm)*	*Crystal Structure*	*Electro-nega-tivity*	*Valence*
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. 118, *Callister & Rethwisch 8e.*

Impurities in Solids

- Specification of composition
  - weight percent

$$C_1 = \frac{m_1}{m_1 + m_2} \text{ x } 100$$

m_1 = mass of component 1

m_2 = mass of component 2

  - atom percent

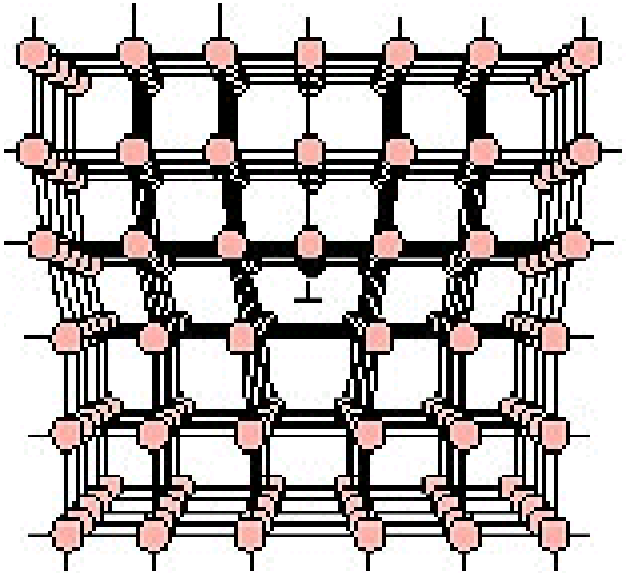
$$C_1' = \frac{n_{m1}}{n_{m1} + n_{m2}} \text{ x } 100$$

n_{m1} = number of moles of component 1

n_{m2} = number of moles of component 2

LINE DEFECTS

- Line defects are the irregularities or deviations from ideal arrangement in entire rows of lattice points.



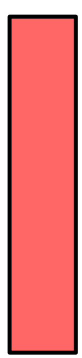
- Interatomic bonds significantly distorted in immediate vicinity of dislocation line.
- Dislocation affects the mechanical properties.

Line Defects

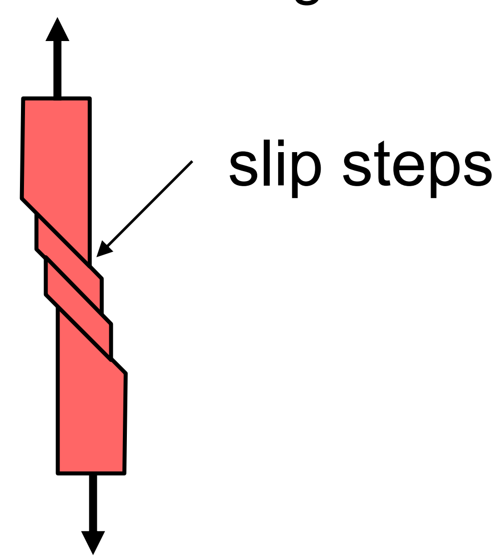
Dislocations:

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

- before deformation



- after tensile elongation



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
  - **b** perpendicular (⊥) to dislocation line
- Screw dislocation:
  - spiral planar ramp resulting from shear deformation
  - **b** parallel (||) to dislocation line

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

Imperfections in Solids

Edge Dislocation

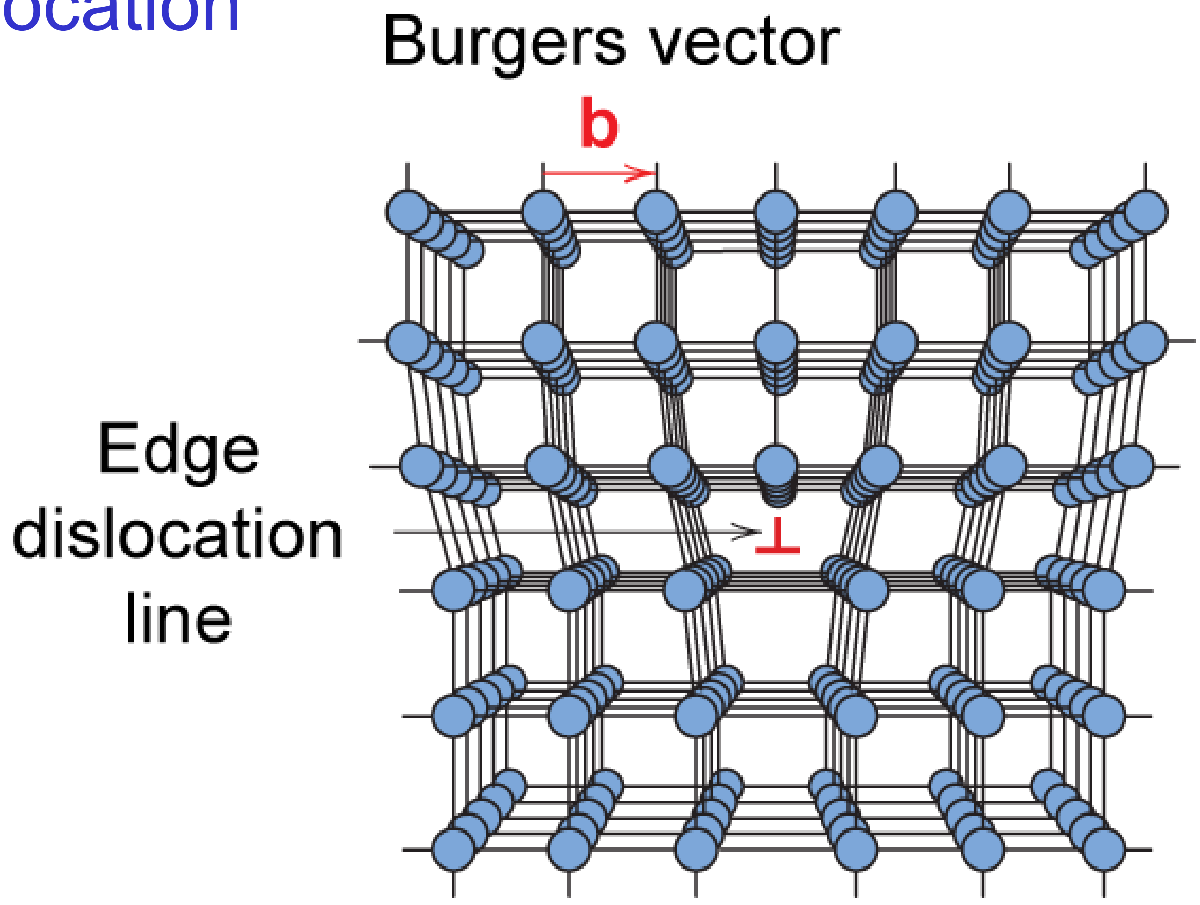
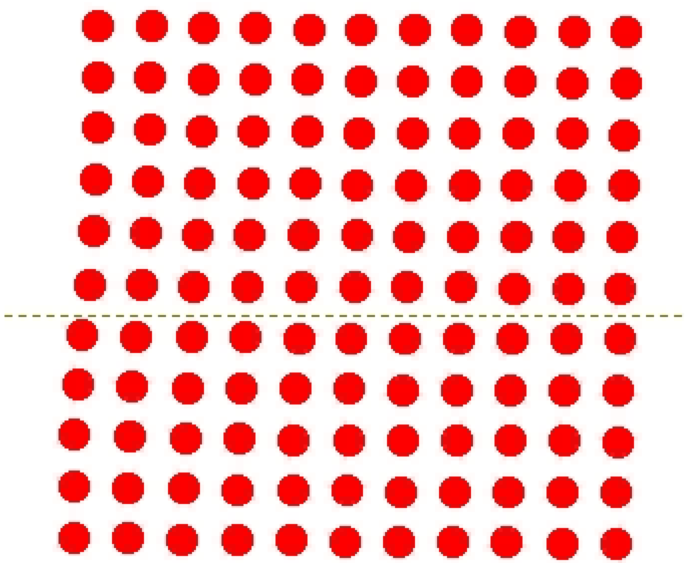


Fig. 4.3, *Callister & Rethwisch 8e.*

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.



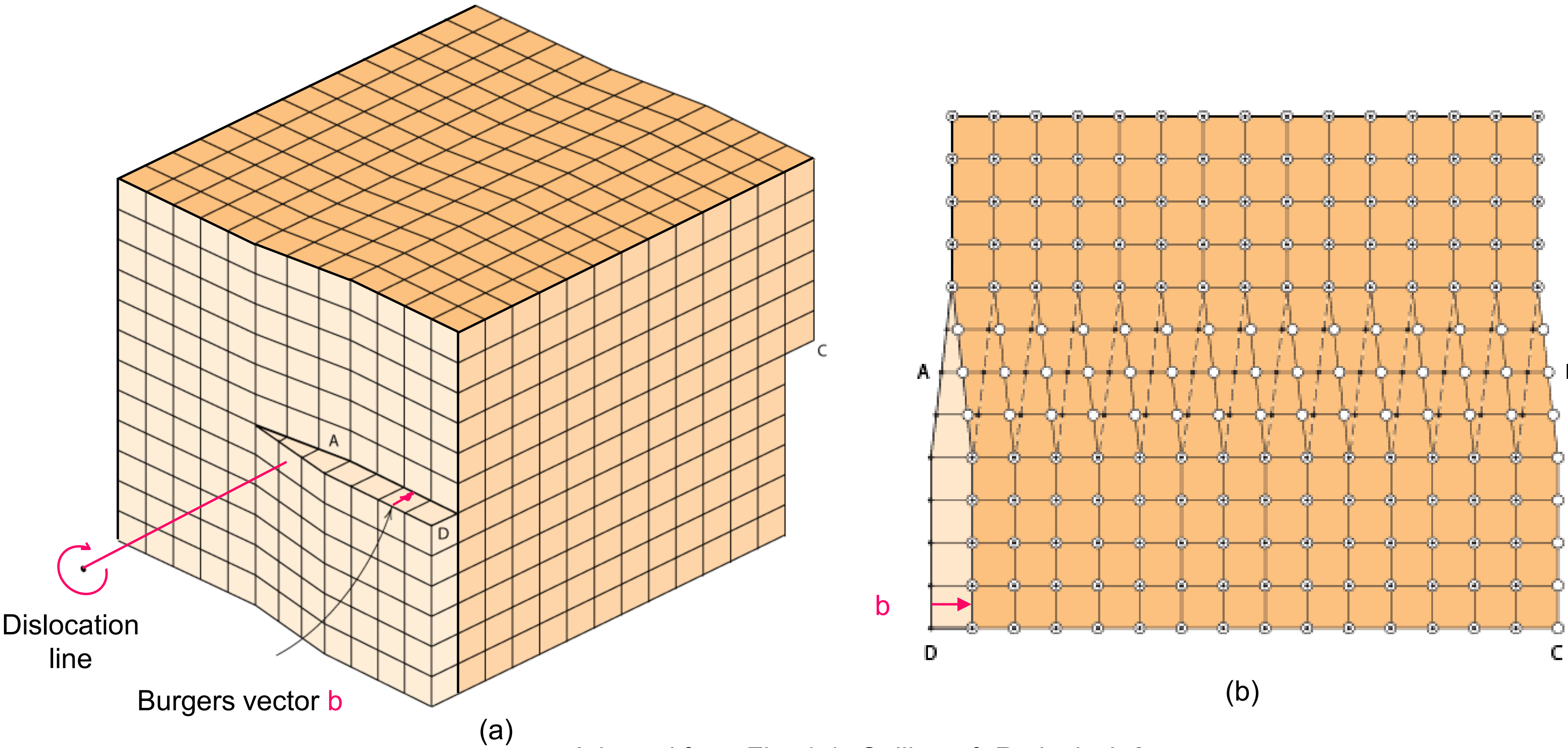
Click once on image to start animation

(Courtesy P.M. Anderson)

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

Imperfections in Solids

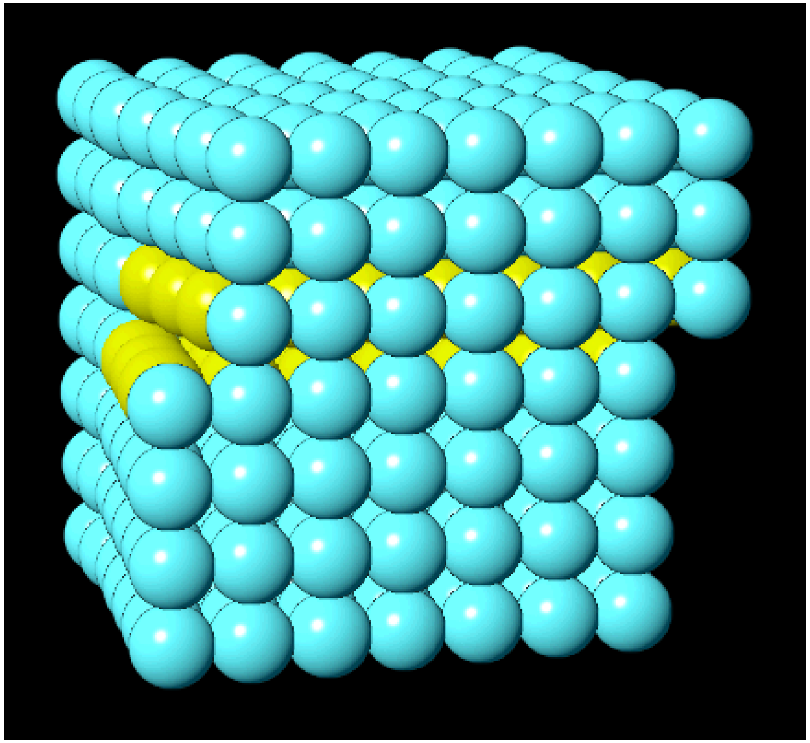
Screw Dislocation



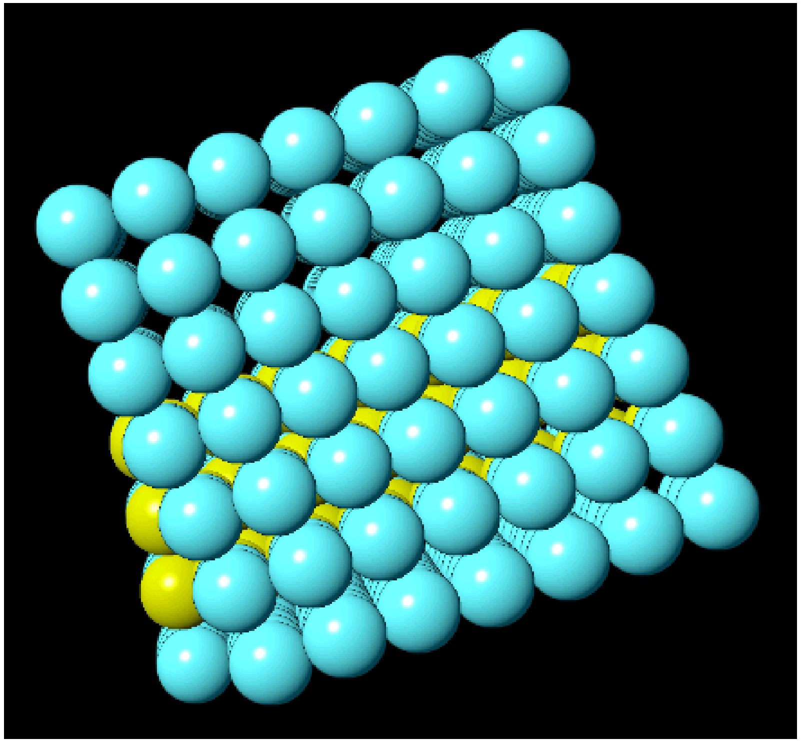
Adapted from Fig. 4.4, *Callister & Rethwisch 8e.*

VMSE: Screw Dislocation

- In VMSE: https://drbuc2jl8158i.cloudfront.net/VMSE/index.html
  - a region of crystal containing a dislocation can be rotated in 3D
  - dislocation motion may be animated



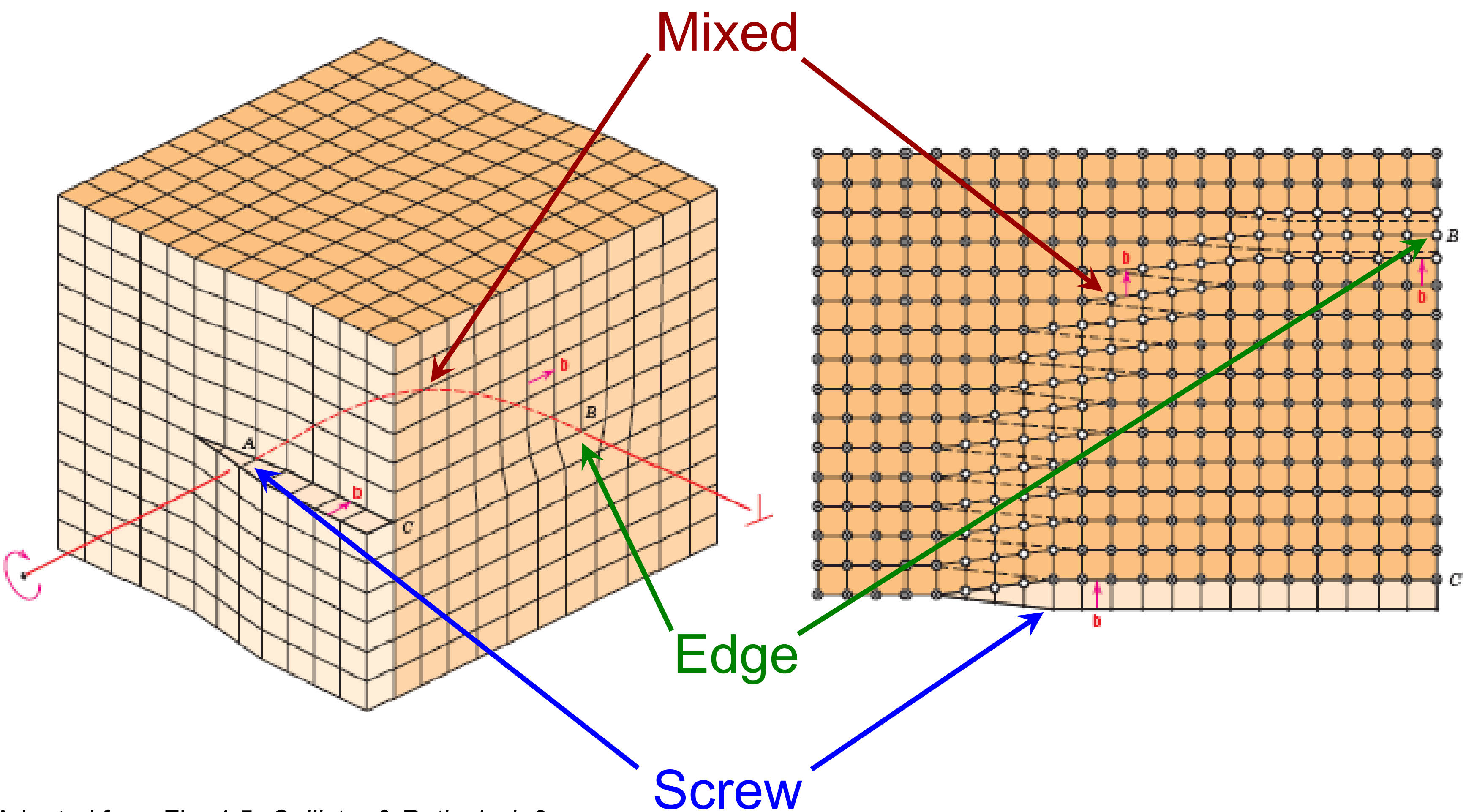
Front View



Top View

VMSE Screen Shots

Edge, Screw, and Mixed Dislocations



Adapted from Fig. 4.5, *Callister & Rethwisch 8e.*

Imperfections in Solids

Dislocations are visible in electron micrographs

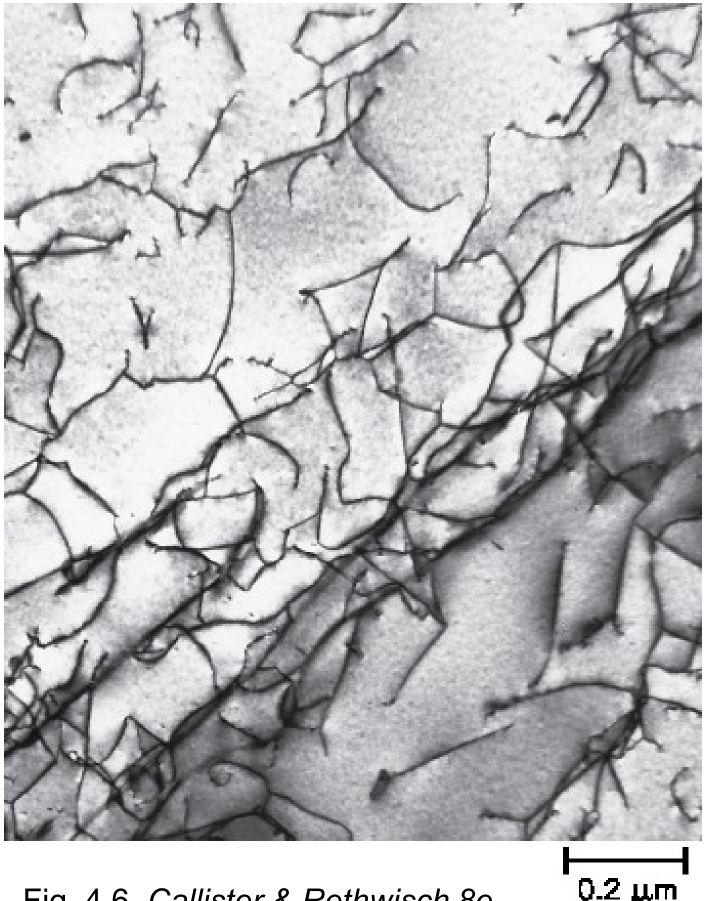
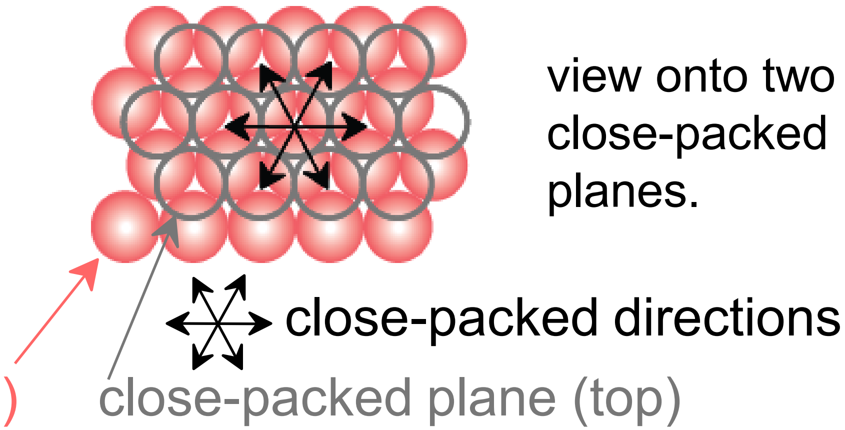


Fig. 4.6, *Callister & Rethwisch 8e.*

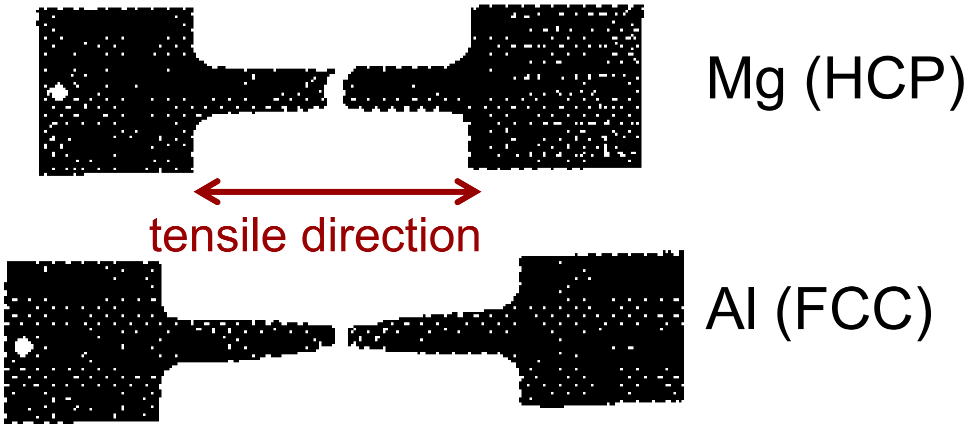
Dislocations & Crystal Structures

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



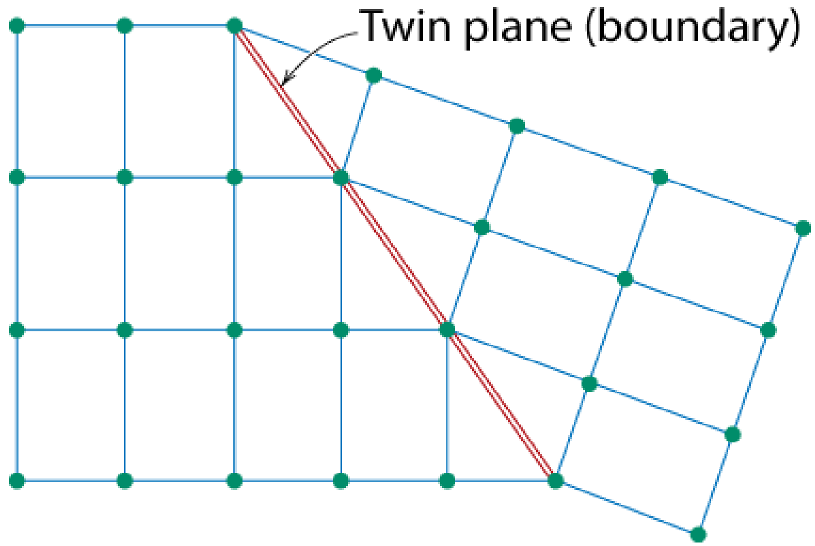
- Comparison among crystal structures:
  FCC: many close-packed planes/directions;
  HCP: only one plane, 3 directions;
  BCC: none

- Specimens that were tensile tested.



Planar Defects in Solids

- One case is a twin boundary (plane)
  - Essentially a reflection of atom positions across the twin plane.



Adapted from Fig. 4.9, *Callister & Rethwisch 8e.*

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

SURFACE DEFECTS

- Surface defects are associated with boundaries that are separate regions of the materials and have different crystal structure.
- Two Dimensional defect.
- Due to change in orientation of the atomic planes and stacking sequence of atomic planes.
- Caused during solidification or mechanical or thermal treatment of material.
- Effect the mechanical properties, electrical resistance and corrosion resistance.

Catalysts and Surface Defects

- A catalyst increases the rate of a chemical reaction without being consumed
- Active sites on catalysts are normally surface defects

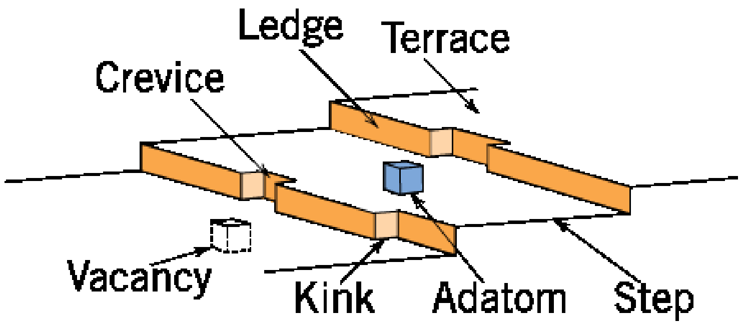


Fig. 4.10, *Callister & Rethwisch 8e.*

Single crystals of $(Ce_{0.5}Zr_{0.5})O_2$ used in an automotive catalytic converter

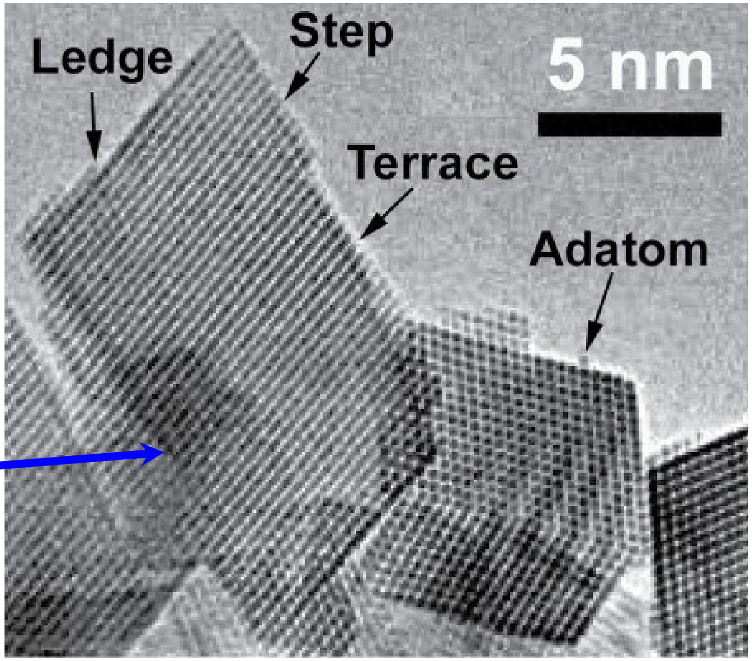
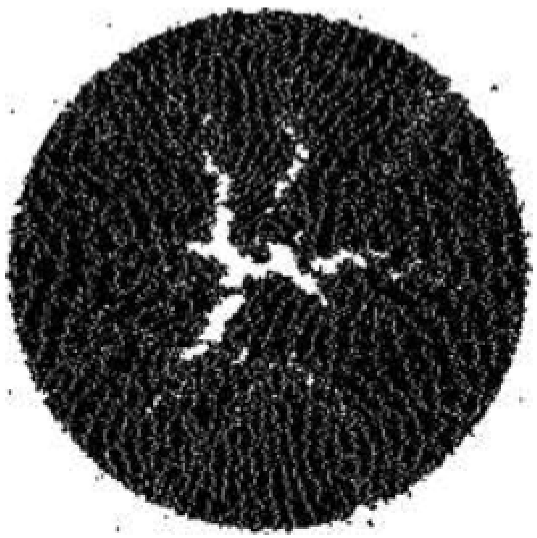


Fig. 4.11, *Callister & Rethwisch 8e.*

Bulk or Volume Defects

- **PERCIPITATES** : Fraction of a micron in size
- **DISPERSANTS** : may be large precipitates, grains, or polygranular particles distributed through microstructure
- **INCLUSIONS** : foreign particles or large precipitate particles ; undesirable ; harmful
- **VOIDS** : Trapped Gases ; Decreases mechanical strength



Cluster of microcracks in a melanin granule irradiated by a short laser pulse.

Effects of Imperfections

- **Mechanical Properties**: Imperfections can either strengthen or weaken materials. For instance, dislocations allow materials to deform more easily, which can enhance ductility. However, too many dislocations or other imperfections can reduce strength.

- **Electrical Properties**: The presence of defects can affect the flow of electrons and influence the conductivity of materials. For instance, vacancies and interstitials can act as scattering centers for electrons.

- **Thermal Properties**: Defects can influence thermal conductivity. For example, grain boundaries can scatter phonons, which are carriers of heat, thus affecting thermal conductivity.

- **Chemical Properties**: Defects can also affect the chemical reactivity of materials, influencing processes like corrosion and oxidation.

Visualization of Imperfections in Solids

1. **Atomic Scale Visualization**
   - ✓ **Scanning Tunneling Microscope (STM)**: This technique provides atomic-level resolution and can image individual atoms and defects on a surface. It’s particularly useful for studying point defects and surface imperfections.
   - ✓ **Atomic Force Microscope (AFM)**: AFM can map surfaces with atomic resolution and provide three-dimensional images of surfaces, revealing features like vacancies, interstitials, and surface roughness.
2. **Microscopic Techniques**
   - ✓ **Transmission Electron Microscopy (TEM)**: TEM can visualize defects such as dislocations, grain boundaries, and stacking faults in thin samples. It offers high-resolution images and can be used to analyze internal structures.
   - ✓ **Scanning Electron Microscopy (SEM)**: SEM provides detailed images of surface features and can be used to observe larger-scale imperfections like grain boundaries and inclusions.

Visualization of Imperfections in Solids

3. **X-Ray Diffraction (XRD)**
   - ✓ **XRD**: This technique is used to identify and analyze crystal structures and can help detect defects by analyzing the diffraction pattern of X-rays scattered by the crystal lattice. Changes in the diffraction pattern can indicate the presence of dislocations, stacking faults, or strain.
4. **Modeling and Simulations**
   - ✓ **Computer Simulations**: Techniques like molecular dynamics (MD) and density functional theory (DFT) can model and simulate the behavior of imperfections in solids. These simulations help visualize how defects interact with the lattice and influence material properties.
   - ✓ **Crystal Structure Models**: Software tools can generate three-dimensional models of crystal structures with defects. These models can illustrate point defects, dislocations, and grain boundaries in a visual and interactive manner.

Visualization of Imperfections in Solids

5. Physical Experiments
   - ✓ **Etching Techniques**: Chemical or electrolytic etching can reveal dislocations and grain boundaries on the surface of a material. By selectively etching the surface, these defects become visible under optical or electron microscopy.
   - ✓ **Deformation Experiments**: Applying stress or strain to a material can make certain defects, like dislocations, more visible as they move and interact within the lattice. This can be observed using microscopy techniques.
6. Visualization in Materials Science
   - ✓ **Defect Maps**: In materials science literature, diagrams and maps often show how different types of defects (e.g., vacancies, dislocations) are distributed in a material. These are useful for understanding the spatial arrangement and interaction of defects.
   - ✓ **Schematic Diagrams**: For educational purposes, schematic diagrams and illustrations are used to represent various defects. These diagrams abstract complex concepts into simpler visual forms, such as showing an edge dislocation as a half-plane of atoms.

Visualization of Imperfections in Solids

7. Software Tools

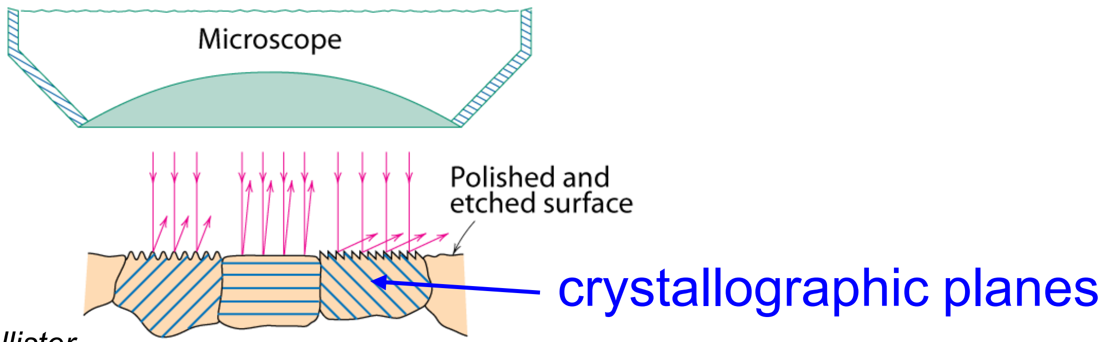
- ✓ **Crystallography Software**: Tools like VESTA or CrystalMaker allow users to create and manipulate crystal structures, including various types of defects. These visualizations can be rotated and zoomed to better understand the spatial arrangement of defects.
- ✓ **Material Science Simulation Software**: Software packages such as LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) or COMSOL Multiphysics can simulate and visualize the effects of imperfections in materials.

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 & Rethwisch 8e.* (Fig. 4.13(c) is courtesy of J.E. Burke, General Electric Co.)

Micrograph of brass (a Cu-Zn alloy)

Optical Microscopy

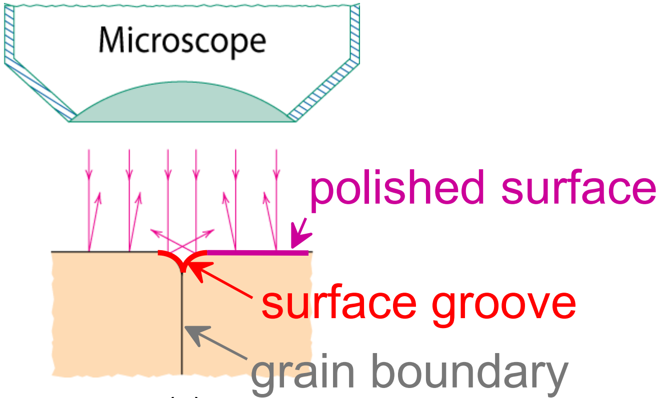
Grain boundaries...

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

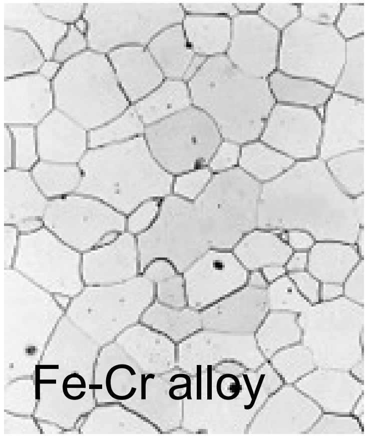
ASTM grain size number

$N = 2^{n-1}$

number of grains/in^2 at 100x magnification



(a)



(b)

Adapted from Fig. 4.14(a) and (b), *Callister & Rethwisch 8e.* (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].)

Optical Microscopy

- Polarized light
  - metallographic scopes often use polarized light to increase contrast
  - Also used for transparent samples such as polymers

Microscopy

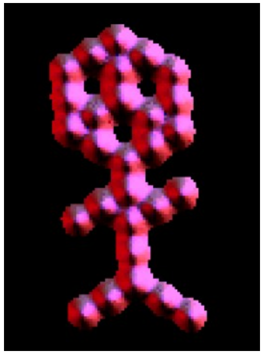
Optical resolution ca. 10^{-7} m = 0.1 μm = 100 nm

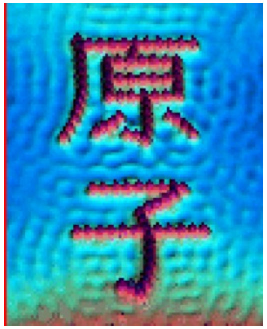
For higher resolution need higher frequency

- 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.

Scanning Tunneling Microscopy (STM)

- Atoms can be arranged and imaged!





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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 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.)

Summary

Defects may be good or bad, depending on whether plastic deformation is desirable or not.

1. Point Defects

Point defects are localized disturbances in the crystal lattice. They include:

- ✓ **Vacancies**:
- ✓ **Interstitials**:
- ✓ **Substitutional Defects**:
- ✓ **Frenkel Defects**:
- ✓ **Schottky Defects**:

2. Line Defects

Line defects, or dislocations, are linear disruptions in the lattice structure:

- ✓ **Edge Dislocations**:
- ✓ **Screw Dislocations**:
- ✓ **Mixed Dislocations**:

Summary

3. Planar Defects

Planar defects involve disruptions over a plane of atoms:

- ✓ **Grain Boundaries**:
- ✓ **Stacking Faults**:
- ✓ **Twin Boundaries**:

4. Volume Defects

Volume defects involve larger-scale disruptions within the material:

- ✓ **Porosity**:
- ✓ **Inclusions**:

Visualizing imperfections in solids often involves a combination of advanced microscopy techniques, computer simulations, and schematic diagrams. Each method provides different levels of detail and insight into how these imperfections affect material properties. By using these tools, researchers and engineers can gain a deeper understanding of material behavior and improve the design and application of various materials.