

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 materials' properties?
- Are defects undesirable?

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Defects by Dimension

- **Zero dimensional (point defects): vacancies, interstitial atoms, substitutional atoms.**
- **One dimensional (linear defects): Mistakes in stacking planes of atoms. A plane of atoms ends in a line. Dislocations.**
- **Two dimensional (planar or areal defects) surfaces and grain boundaries.**
- **Three dimensional: Second phases.**

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Why do we care about defects?

Many properties may be altered by defects/impurities.

e.g.

1) **Mechanical properties:** Metal alloys for improving strength.

2) **Electrical properties:**

- Defects and impurities can reduce metal conductivity.
- Doping in semiconductorsto control of conductivity.

3) **Optical properties:**

- Wavelengths of light being absorbed and/or emitted by materials can be altered with imperfections.

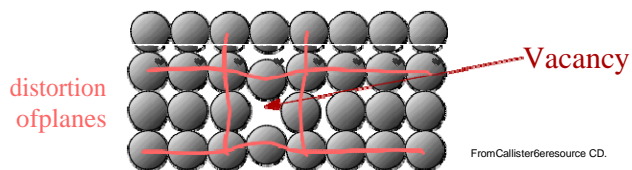
Mn-doped ZnSe quantum dots.



and many more examples....

Point Defects

1. **Vacancies:** missing atoms from lattice sites.



Vacancies will also cause missing bonds (costs energy to create vacancies).

Why should vacancies form?

Consider the energy required to create a vacancy.

Q_v = Activation energy to create vacancy

Where does the energy to overcome Q_v come from?

Thermal Energy!
 k = Boltzmann constant

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

No. of vacancies

Total No. of lattice sites

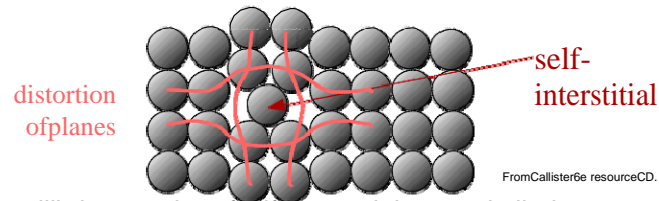
N_v depends on temperature!

Typically: $\frac{N_v}{N} \sim 10^{-4}$

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Point Defects

2. **Self-interstitial**: an extra atom (of the same type as the lattice atoms) placed in between lattice sites.



For equilibrium number of self-interstitials: treat similarly as vacancies.

$$N_s = N \exp\left[-\frac{Q_s}{kT}\right]$$

Self-interstitials are usually not as highly probable as vacancies.

WHY?

Typically, interstitial sites are much smaller than lattice atoms.

Self-interstitials would likely introduce significantly larger distortions!

i.e. $Q_s \gg Q_v$

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Point defects: example problem

Calculate the equilibrium number of vacancies for a cubic centimeter of copper at 1000°C.

$$Q_v = 0.9 \text{ eV/atom}$$

$$A = 63.5 \text{ g/mol}$$

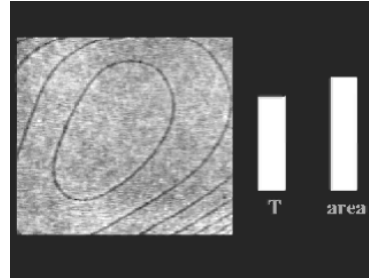
$$d = 8.4 \text{ g/cm}^3$$

$$k = 1.38 \times 10^{-23} \text{ J/K} = 8.62 \times 10^{-5} \text{ eV/K}$$

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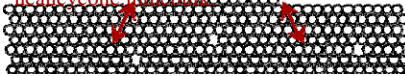
Observing equilibrium vacancy concentration

- 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



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



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Impurities in solids

1. In the limit of small number of impurities: consider as point defects.
2. When there is a large amount: consider a **solution**.
Many familiar materials are highly impure (e.g. metal alloys).

Solid solutions

Homogeneous distribution of impurities (similar to liquid solutions) with the crystal structure of the host material maintained.

Solvent: element or compound that is most abundant (host atoms).

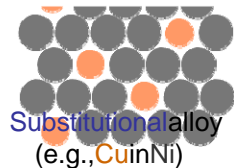
Solute: element or compound present in minor concentration (impurity).

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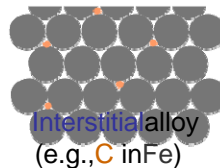
Point defects in alloys

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

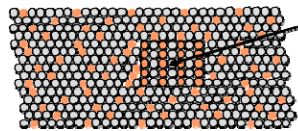
- **Solid solution of B in A** (i.e., random dist. of point defects)



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.

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Solubility for solid solutions

A. Solubility of **substitutional solution** will depend on:

1. **Atomic size factor:** typically, atomic radii difference < 15%.
Too large or too small impurity atoms will cause too much lattice distortions!
2. **Crystal structure:** For appreciable solubility, host and impurity atoms should have the same crystal structure.
3. **Electronegativity:** Too large electronegativity difference will lead to intermetallic compounds rather than solutions.
4. **Valence:** Same valence is preferred for high solubility.

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Example
Is solid-solution favorable, or not?

• **Si-Ge Alloys**

Rule 1: $r_{\text{Si}} = 0.117 \text{ nm}$ and $r_{\text{Ge}} = 0.122 \text{ nm}$.
 $\Delta R\% = 4\%$

favorable ✓

Rule 2: Si and Ge have the diamond crystal structure. **favorable** ✓

Rule 3: $E_{\text{Si}} = 1.90$ and $E_{\text{Ge}} = 2.01$. Thus, $\Delta E\% = 5.8\%$ **favorable** ✓

Rule 4: Valency of Si and Ge are both 4. **favorable** ✓

Expect Si and Ge to form S.S. over wide composition range.

In fact, solid solution forms over entire composition at high temperature.

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Example
Is solid-solution favorable, or not?

• **Cu-Ag Alloys**

Rule 1: $r_{\text{Cu}} = 0.128 \text{ nm}$ and $r_{\text{Ag}} = 0.144 \text{ nm}$.
 $\Delta R\% = 9.4\%$

favorable ✓

Rule 2: Ag and Cu have the FCC crystal structure. **favorable** ✓

Rule 3: $E_{\text{Cu}} = 1.90$ and $E_{\text{Ni}} = 1.80$. Thus, $\Delta E\% = -5.2\%$ **favorable** ✓

Rule 4: Valency of Cu is +2 and Ag is +1. **NOT favorable**

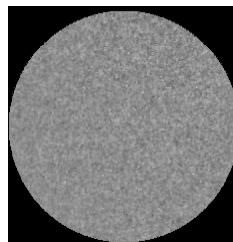
Expect Ag and Cu to have limited solubility.

In fact, the Cu-Ag phase diagram (T vs. c) shows that a solubility of only 18% Ag can be achieved at high T in the Cu-rich alloys.

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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.



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Solubility for solid solutions

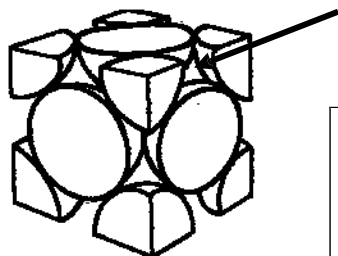
B. Interstitial solutions:

Largedifferenceinatomicradiiisusuallyrequired.

MostmetalshaveclosepackingwithrelativelylargeAPF.

(e.g. $APF_{FCC} = APF_{HCP} = 0.74$. that means 74% of the space is filled!)

Onlysmallatomswill fit into these small interstitial sites without requiring high energies.



e.g. $C_{in}Fe$:

$R_C = 0.071 \text{ nm}$

$R_{Fe} = 0.124 \text{ nm}$

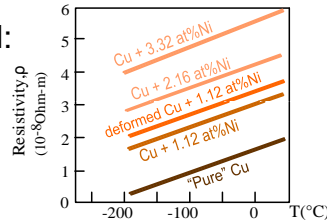
Even with this largedifference max.

conc. is only ~2% $C_{in}Fe$

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Effects of Composition in Solid Solutions

Electrical:



Mechanical: Strengthening (a major purpose of making alloys)

and many more effects...

Composition can change Phases/Structure which in turn determine properties!

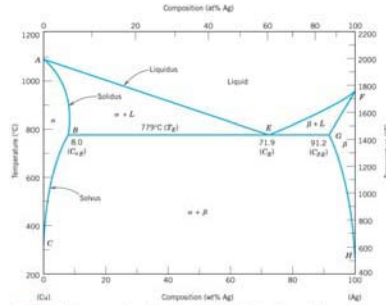
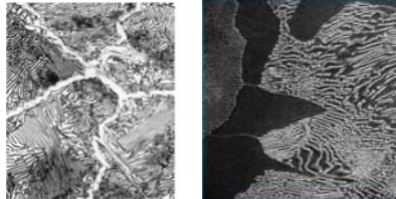


Fig. 9.16 The copper-silver phase diagram. [Adapted from Binary Alloy Phase Diagrams, 2nd edition, Vol. 1, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]

Composition Specification

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

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

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

• Basis for conversion:

$$\frac{\text{mass of B}}{\text{mass of A}} = \frac{\text{moles of B}}{\text{moles of A}} \times \frac{A_B}{A_A}$$

\swarrow atomic weight of B
 \nwarrow atomic weight of A

Example problem: conversion

- Determine the composition in at% of an alloy with 80wt% Al and 20wt% Cu

$$A_{Al} = 26.98 \text{ g/mol}$$

$$A_{Cu} = 63.55 \text{ g/mol}$$

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Average alloy density

$$\rho_{avg} = \frac{\text{total mass}}{\text{total volume}} = \frac{m_A + m_B}{V_A + V_B}$$

$$\text{With } V_A = \frac{m_A}{\rho_A} \text{ and } V_B = \frac{m_B}{\rho_B}$$

$$\rho_{avg} = \frac{m_A + m_B}{m_A/\rho_A + m_B/\rho_B}$$

In terms of wt% and at%:

$$\rho_{avg} = \frac{100}{\frac{C_A}{\rho_A} + \frac{C_B}{\rho_B}}$$

$$\rho_{avg} = \frac{C_A^A \rho_A + C_B^B \rho_B}{C_A^A + C_B^B}$$

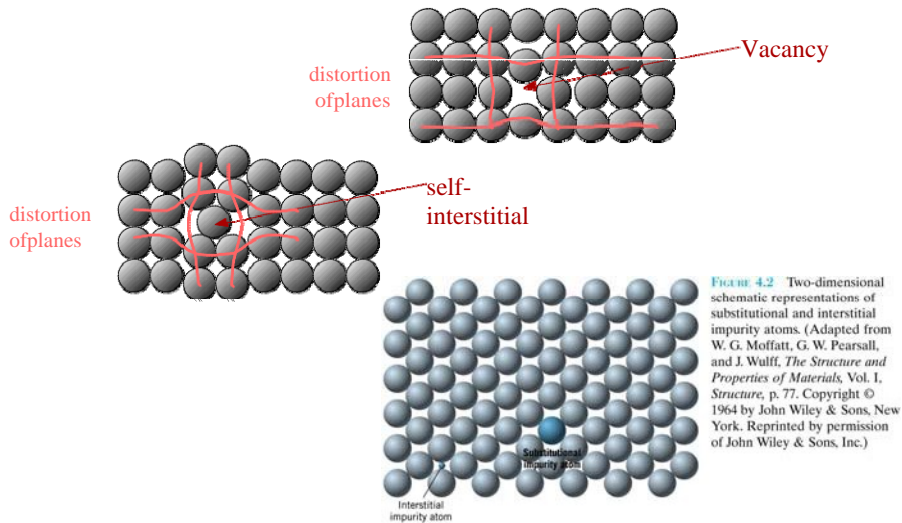
A A B B

A A A B B B

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Imperfections in ionic solids

Recall point defects in solids....

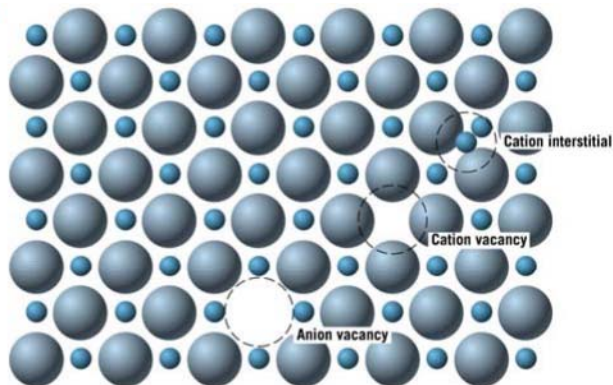


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Imperfections in ionic solids

Point defects also possible in ionic solids. But...?

FIGURE 12.20
Schematic representations of cation and anion vacancies and a cation interstitial. (From W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. 1, *Structure*, p. 78. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

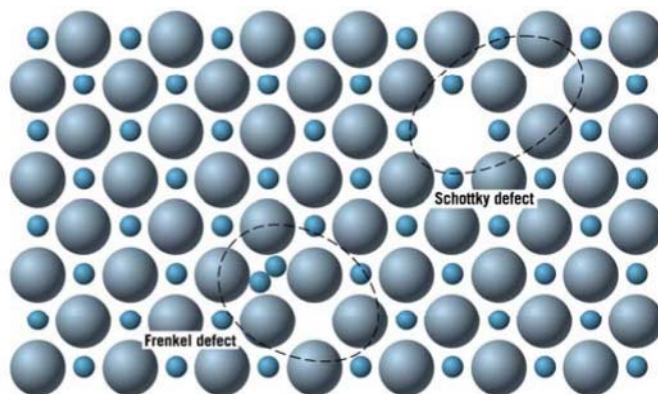


Charge neutrality need to be met!

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Imperfections in ionic solids

FIGURE 12.21
Schematic diagram showing Frenkel and Schottky defects in ionic solids. (From W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. 1, *Structure*, p. 78. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)



Can we have a Frenkel defect of anions?

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Example problem

1. When a Ca^{2+} is substituted for a Na^+ ion in a NaCl crystal, what point defects are possible and how many of these defects exist for every Ca^{2+} ion?
2. What point defects are possible for MgO as impurity in Al_2O_3 and how many Mg^{2+} ions must be added to form each of these defects?

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Linear Defects: edge dislocation

Dislocations: Linear defects around which atoms are misaligned

1. Edge dislocation: Linear defect that centers around a line that is defined along the end of an extra plane of atoms

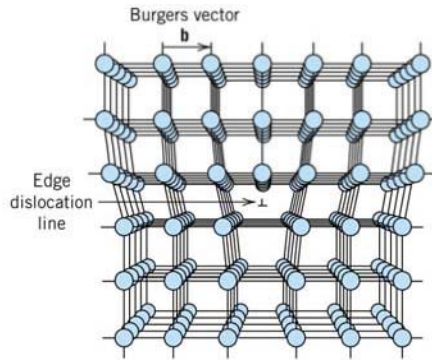


FIGURE 4.3 The atom positions around an edge dislocation; extra half-plane of atoms shown in perspective. (Adapted from A. G. Guy, *Essentials of Materials Science*, McGraw-Hill Book Company, New York, 1976, p. 153.)

Denoted by \perp or \top
 ↙ ↘
 ↖ ↗
 Points to the extra plane of atoms

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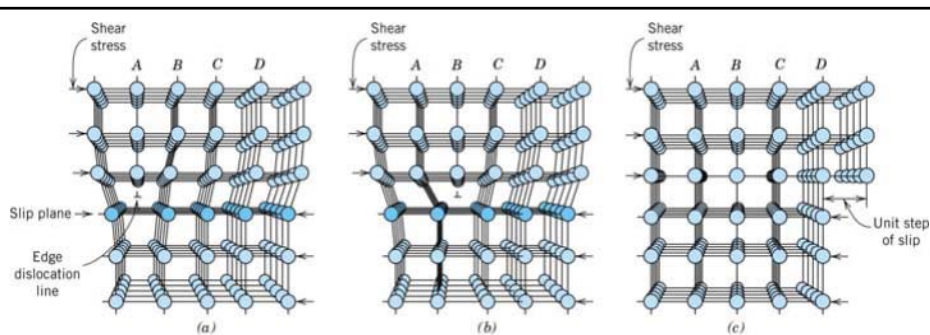


FIGURE 7.1 Atomic rearrangements that accompany the motion of an edge dislocation as it moves in response to an applied shear stress. (a) The extra half-plane of atoms is labeled A. (b) The dislocation moves one atomic distance to the right as A links up to the lower portion of plane B; in the process, the

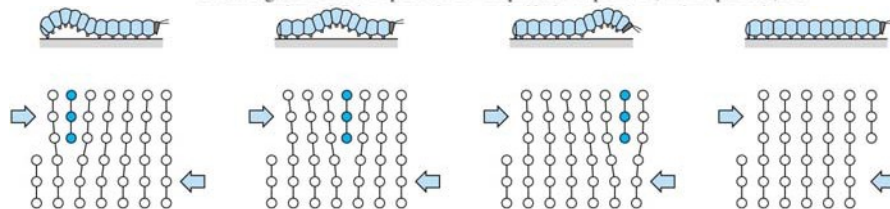
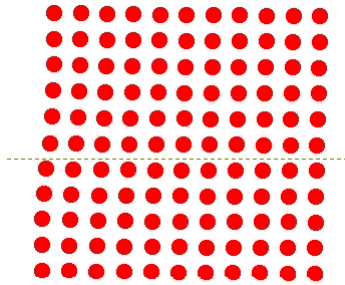


FIGURE 7.3 Representation of the analogy between caterpillar and dislocation motion. 24

Edge dislocation



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

(Courtesy P.M. Anderson)

Note that the edge dislocation causes slip between crystal planes when they move leading to **plastic** (permanent) **deformation**.

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Linear Defects: Screw dislocation

2. **Screw dislocation**: shifted by one atomic distance

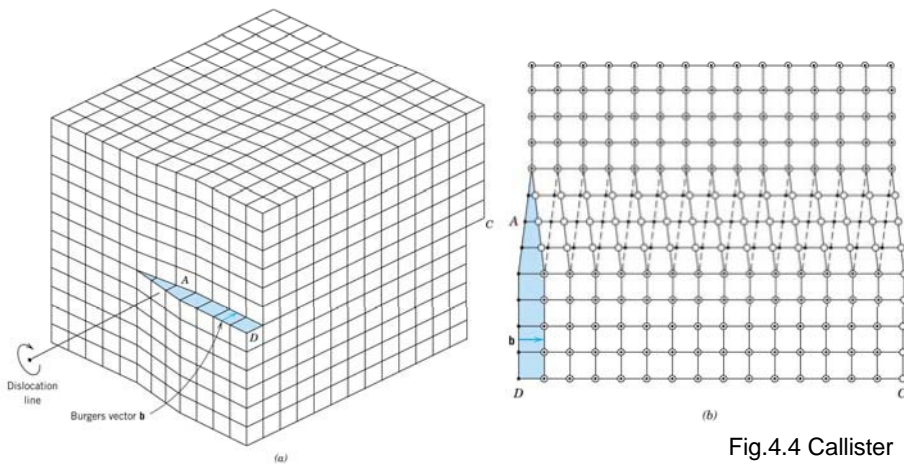
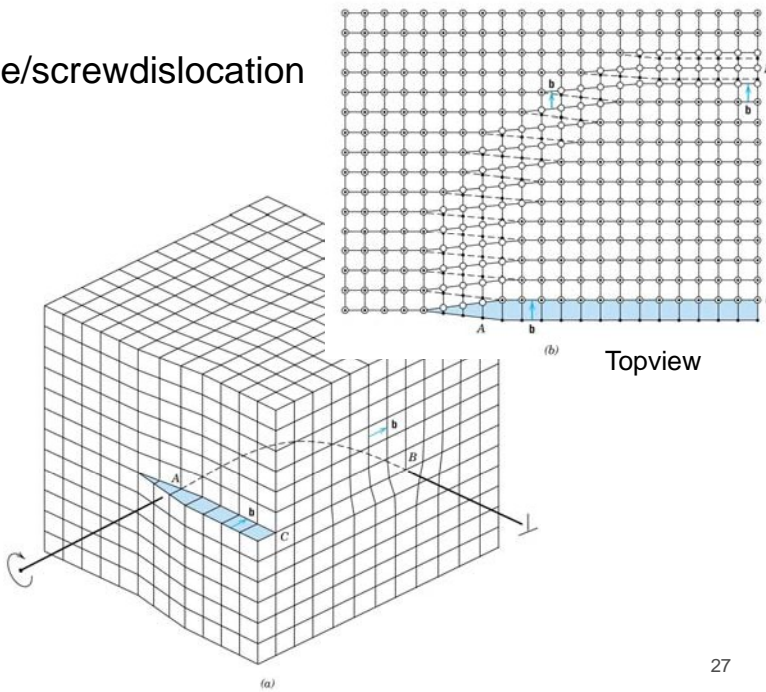


Fig.4.4 Callister

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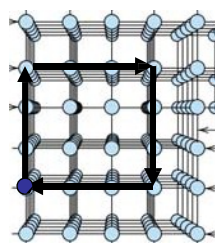
Mixed edge/screw dislocation

FIGURE 4.5
 (a) Schematic representation of a dislocation that has edge, screw, and mixed character. (b) Top view, where open circles denote atom positions above the slip plane. Solid circles, atom positions below. At point A, the dislocation is pure screw, while at point B, it is pure edge. For regions in between where there is curvature in the dislocation line, the character is mixed edge and screw. (Figure b from W. T. Read, Jr., *Dislocations in Crystals*, McGraw-Hill Book Company, New York, 1953.)

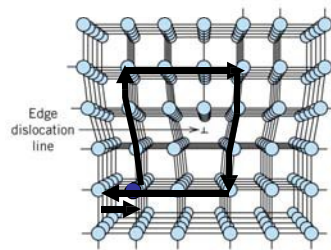


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Burgers Vector



Perfect lattice
 Back at the same atom



With an edge dislocation
 Need to go back an atomic spacing to end at the same atom.

Burgers vector: the magnitude and direction of the lattice distortion associated with dislocations

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Example: Burgers vector

- Find the Burgers vector for a BCC crystal.

Note: Burgers vectors for BCC and FCC can be expressed as

$$\frac{a}{2}[hkl]$$

Lattice parameter Miller index

Calculate the magnitude of Burgers vector for α -Fe (BCC) given that $R_{\text{Fe}} = 0.1241 \text{ nm}$. Compare to the atomic spacing of $2R_{\text{Fe}}$.

Observing dislocations

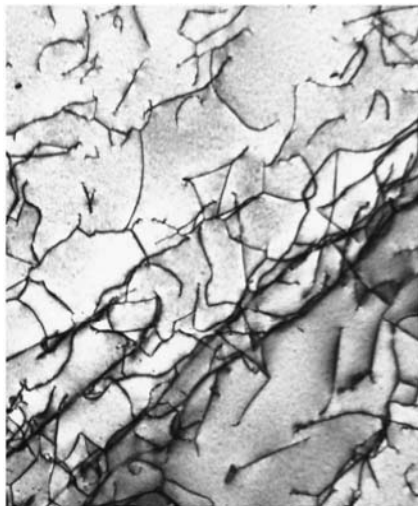


FIGURE 4.6 A transmission electron micrograph of a titanium alloy in which the dark lines are dislocations. 51,450 \times . (Courtesy of M. R. Plichta, Michigan Technological University.)

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Planar Defects

Primary defect types:

Surfaces & Interfaces

- Places where reactions occur and materials mix

Grain Boundaries

- Lattices (and so bonds) do not match up

Twins

- Planes shear to change material shape

Stacking Faults

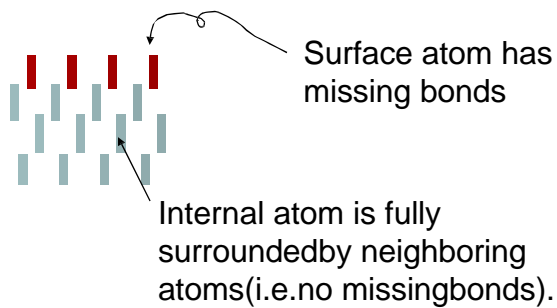
- Errors in stacking (eg: ABCABCABACBACBABCABC)

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External surface

- surface atoms are in higher energy states than internal atoms.

Why?



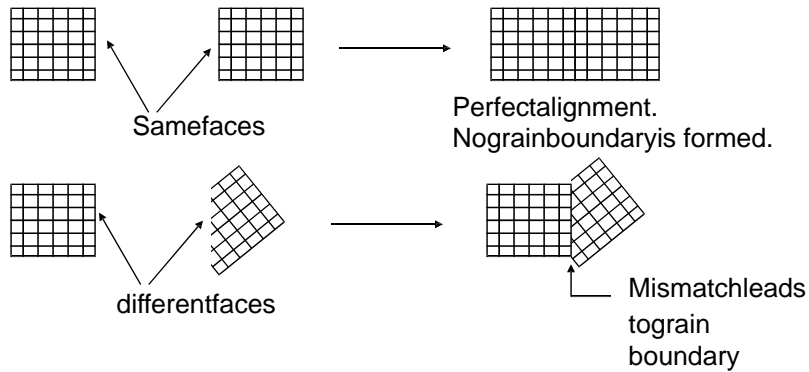
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Grain Boundaries

- 2D defects that separate small grains (crystals having different crystallographic orientations within a polycrystalline material)

single crystal: periodic arrangement of atoms is perfect and extends throughout the crystal.

• **polycrystalline:** composed of many small crystals (grains).



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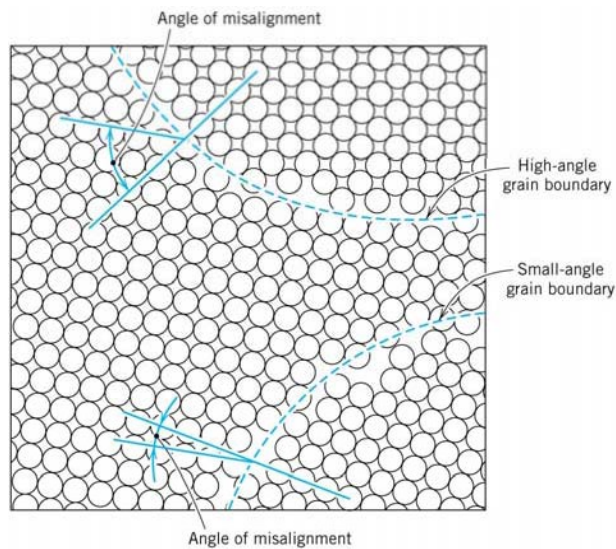
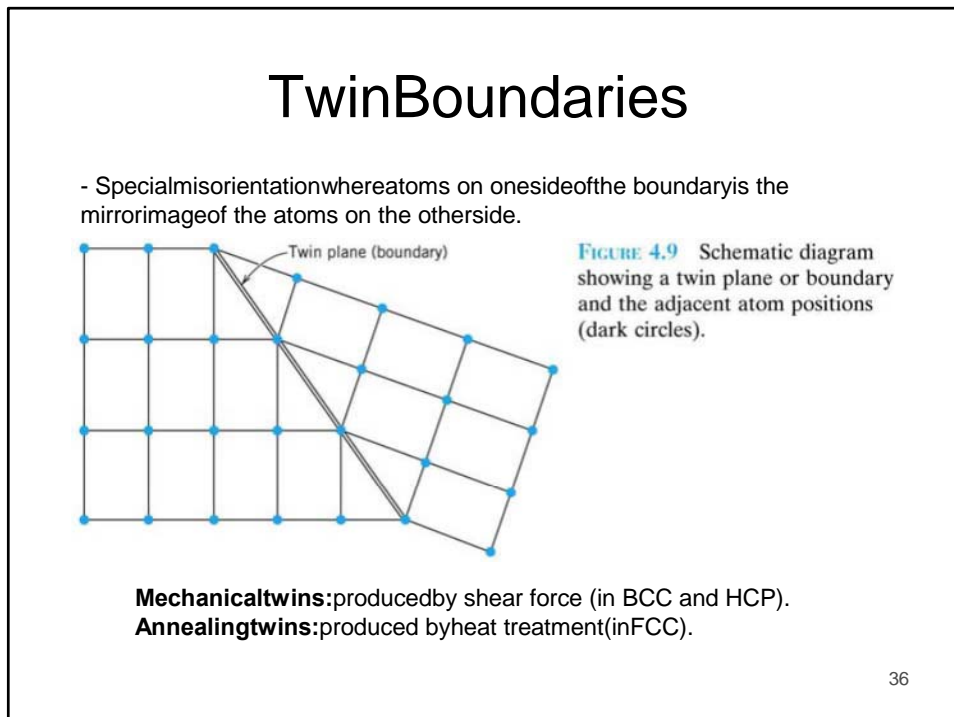
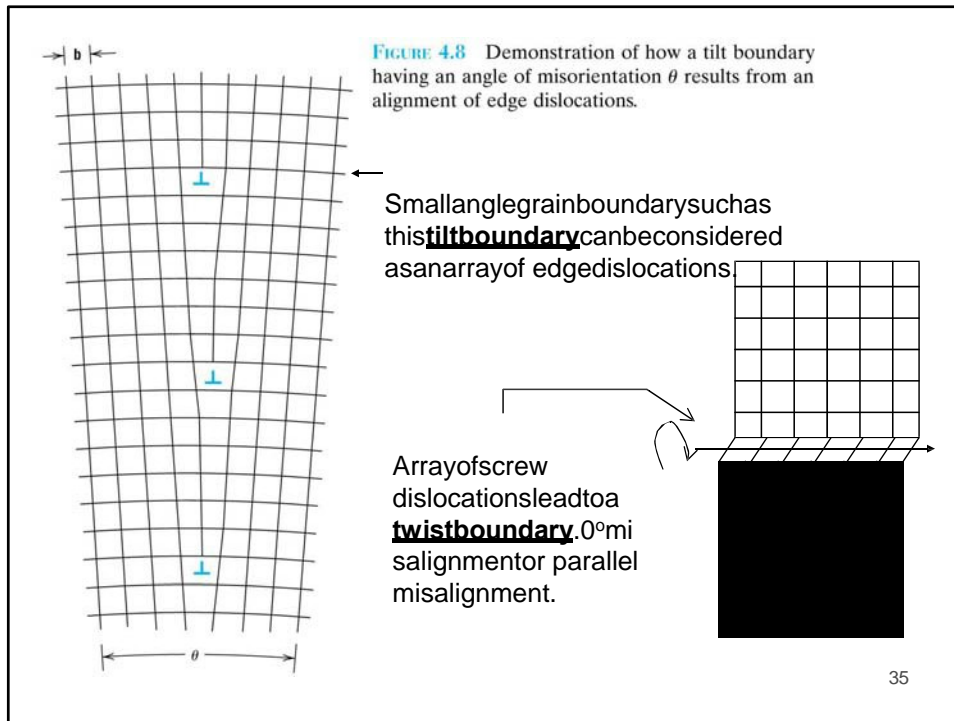


FIGURE 4.7 Schematic diagram showing small- and high-angle grain boundaries and the adjacent atom positions.

Depending on which planes are brought together, the angle of alignment will vary.

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Effects of grain boundaries

Changes in mechanical properties

- Boundaries are good places for fracture to occur
- Boundaries interrupt the movement of dislocations

Changes in electrical properties

- Good places to scatter electrons or inhibit their movement

Sites for atom diffusion

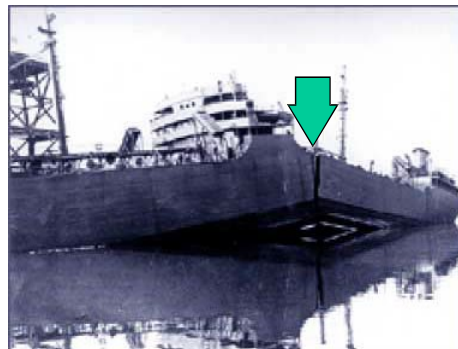
- Diffusing atoms move more easily in the boundaries
- Some atoms like to sit in the boundaries (weaken them)
- Materials can "creep" which means even metals at high temperatures can flow like liquids by diffusion, often through grain boundaries.

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Materials Embrittlement

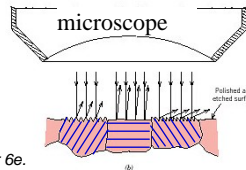
Oops...

A World-war II liberty ship which broke in half due to poor welds. The major problem was sulfur impurities in the iron of the weld which caused weak grain boundaries.



Observing grain boundaries: Optical microscopy

- 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.)

From Callister 6e resource CD.



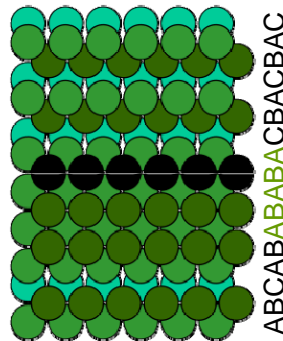
micrograph of
Brass (Cu and Zn)

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Stacking faults

Any time the stacking sequence of atoms makes a difference an error in stacking of atoms can change the properties of the material

Example: stacking faults can convert FCC to HCP structures. Materials of these two structures often contain such faults and many have altered properties as a result.

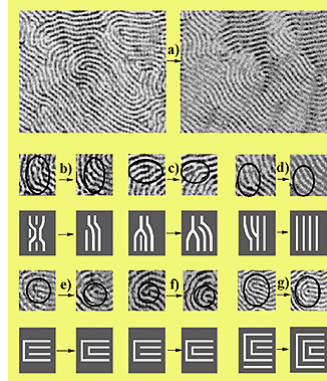


Stacking faults look almost exactly like twins in the electron microscope.

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Imperfections in polymers

- Some are similar to metals and ceramics: e.g. **interstitials** and **vacancies**.
- **Chain ends** can be considered as imperfections since they are different than the repeating units (e.g. initiator attached at end).
- **Amorphous regions** between crystalline regions.
- **Copolymers:**



Defect diffusion in block-copolymers

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Concepts to remember

- **Point defects:** vacancies, self-interstitials, impurities.
- **Solid solutions:** interstitial, substitutional, solubility, and alloy composition and densities.
- **Dislocations:** edge, screw, dislocation motion, and Burgers vector.
- **Grain boundaries and related:** tilt and twist boundaries, surfaces, interfaces, twins, stacking faults, and optical microscopy.
- **Imperfections have very important consequences on the properties of materials.**

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