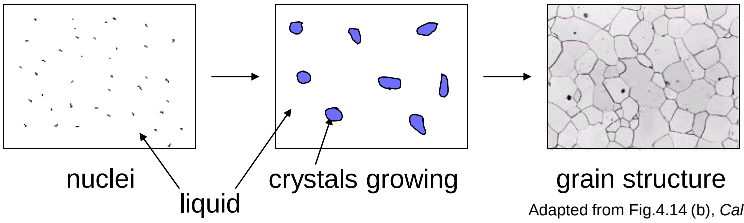
CHAPTER 4:
IMPERFECTIONS IN SOLIDS

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?

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



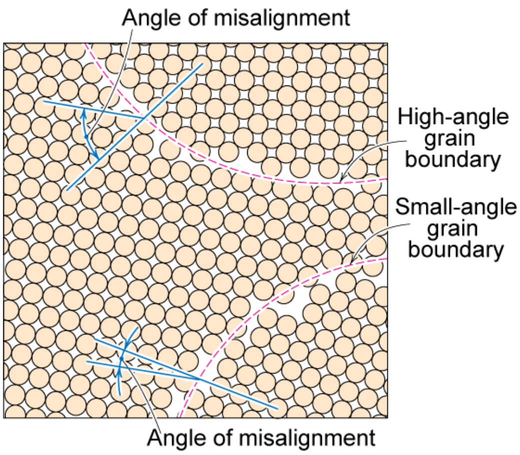
Adapted from Fig.4.14 (b), *Callister 7e.*

- 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

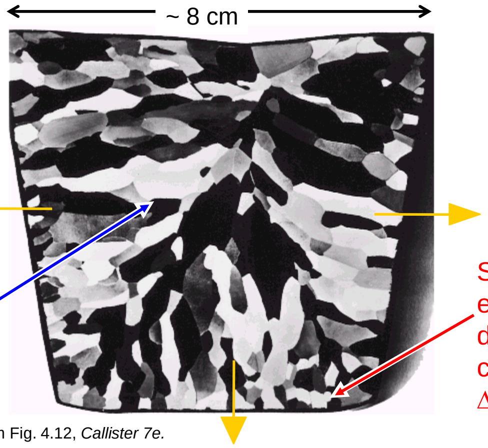


Adapted from Fig. 4.7, *Callister 7e.*

Solidification

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

- columnar (elongated grains)



heat flow

Columnar in area with less undercooling

Shell of equiaxed grains due to rapid cooling (greater ΔT) near wall

Adapted from Fig. 4.12, *Callister 7e.*

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

Imperfections in Solids

There is no such thing as a perfect crystal.

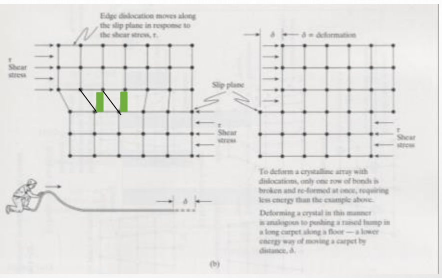
- What are these imperfections?
- Why are they important?

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

Types of Imperfections

• Vacancy atoms	Point defects
• Interstitial atoms	
• Substitutional atoms	
• Dislocations	Line defects
• Grain Boundaries	Area defects

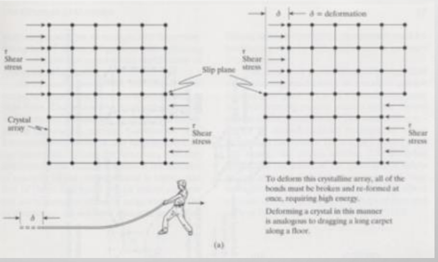
How do Metal Crystals Fail??
Answer: Slip due to dislocations



To deform a crystalline array with dislocations, only one row of bonds is broken and re-formed at once, requiring less energy than the example above.

Deforming a crystal in this manner is analogous to pushing a raised bump in a long carpet along a floor — a lower energy way of moving a carpet by distance, δ.

(b)



To deform this crystalline array, all of the bonds must be broken and re-formed at once, requiring high energy.

Deforming a crystal in this manner is analogous to dragging a long carpet along a floor.

(a)

THEORETICAL STRENGTH OF METAL

- STRENGTH, S_U SHOULD BE APPROXIMATELY E/10 IF BASED ON ATOMIC BOND.
- E/10 = 3,000 KSI FOR STEEL >>> ACTUAL S_U WHICH IS BETWEEN APPROXIMATELY 30 KSI TO 200 KSI
- WHY??????
- DEFECTS!!!

TYPES OF DEFECTS:

- SURFACE DEFECTS
  - GRAIN BOUNDARIES
- POINT DEFECTS
  - VACANCY, SUBSTITUTIONAL (ATOM REPLACES HOST), INTERSTITIAL (ATOM SQUEEZES IN BETWEEN HOST), IMPURITY
- LINE DEFECTS
  - EDGE DISLOCATIONS, SCREW DISLOCATIONS

🟩 = good defect!

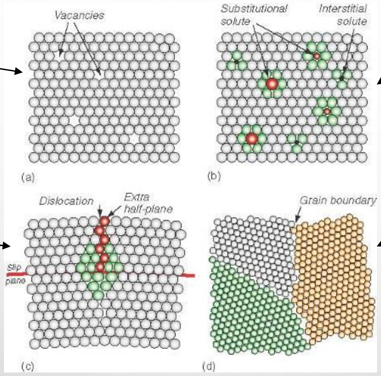
Little impact on strength

Alloying and heat treating

Greatest impact on strength and ductility!!

Course GB = weak,

Fine GB = strong and ductile

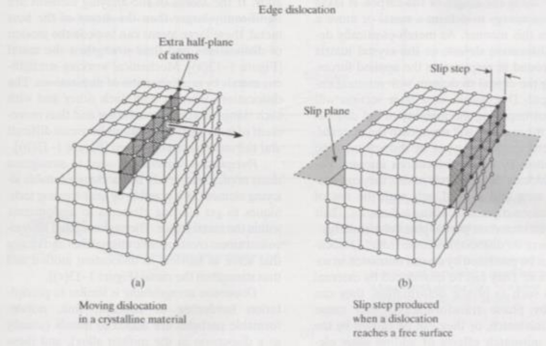


DEFECTS IN CRYSTALS. (A) VACANCIES–MISSING ATOMS. (B) FOREIGN (SOLUTE) ATOM ON INTERSTITIAL AND SUBSTITUTIONAL SITES.

(C) LINE DEFECT = A DISLOCATION–AN EXTRA HALF-PLANE OF ATOMS. (D) GRAIN BOUNDARIES.

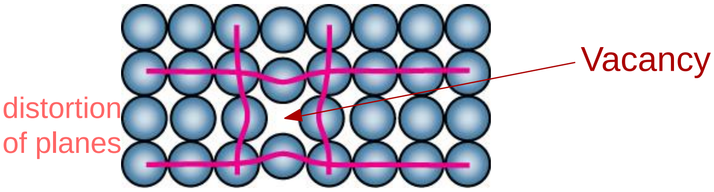
WHAT IS THE MOST SIGNIFICANT DEFECT?

Answer: The line defect (edge dislocation or screw dislocation)

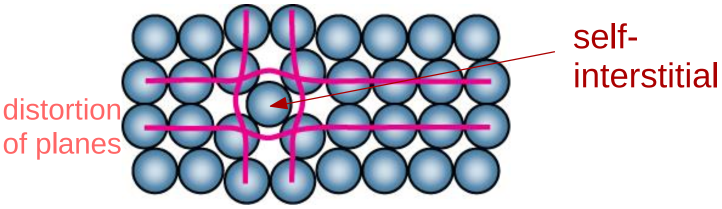


Point Defects

- 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

Activation energy

No. of potential defect sites.

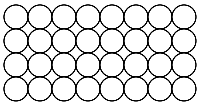
$$\frac{N_v}{N} = \exp\left(\frac{-Q_v}{kT}\right)$$

Temperature

Boltzmann's constant

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

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



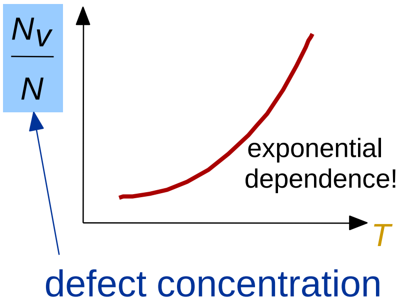
Each lattice site is a potential vacancy site

Measuring Activation Energy

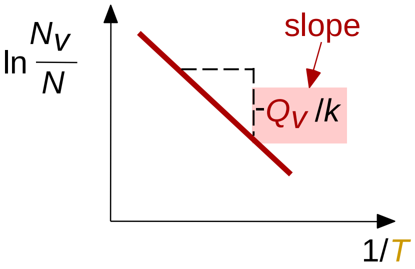
- We can get Q_v from an experiment.

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

- Measure this...



- Replot it...



Estimating Vacancy Concentration

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

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

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

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

0.9 eV/atom

1273K

8.62×10^{-5} eV/atom-K

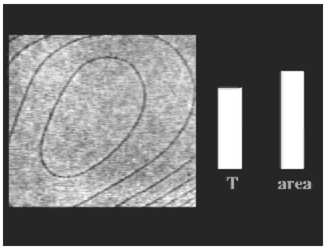
For 1 m^3, $N = \rho \times \dfrac{N_A}{A_{Cu}} \times 1\ m^3 = 8.0 \times 10^{28}$ sites

- Answer:

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

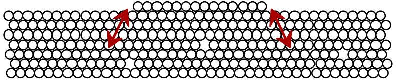
Observing Equilibrium Vacancy Conc.

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



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

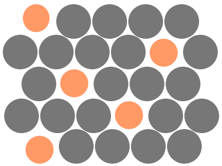
Island grows/shrinks to maintain equil. vancancy conc. in the bulk.



Point Defects in Alloys

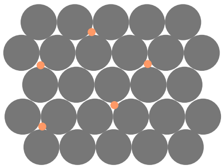
Two outcomes if impurity (B) added to host (A):

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



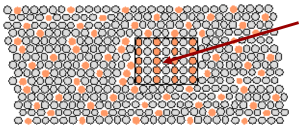
Substitutional solid soln.
(e.g., Cu in Ni)

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.

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

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. 106, *Callister 7e.*

Imperfections 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

  - atom percent

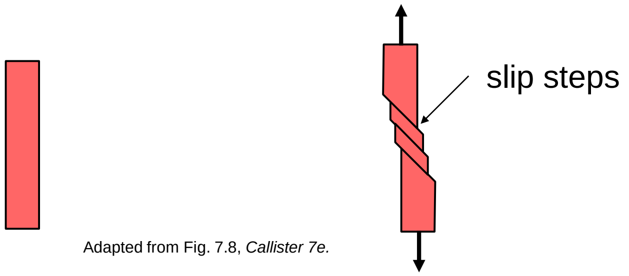
$$C_1^{'} = \frac{n_{m1}}{n_{m1} + n_{m2}} \text{x} \, 100$$

n_{m1} = number of moles of component 1

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

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** ⊥ to dislocation line
- Screw dislocation:
  - – spiral planar ramp resulting from shear deformation
  - – **b** || to dislocation line

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

Imperfections in Solids

Edge Dislocation

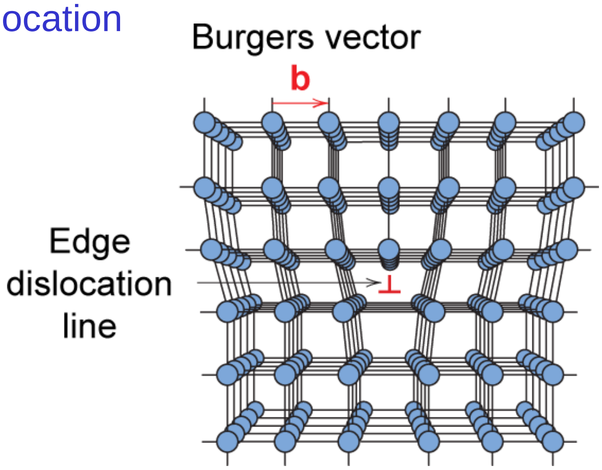
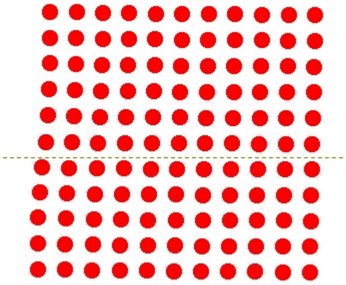


Fig. 4.3, *Callister 7e.*

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.

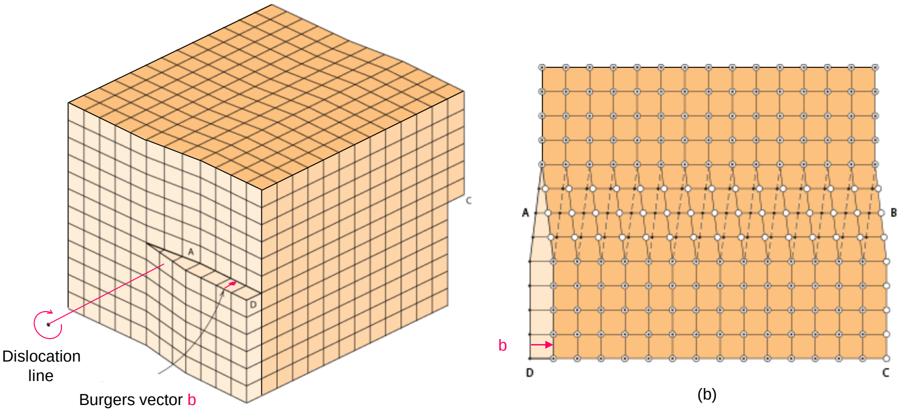


Atomic view of edge dislocation motion from left to right as a crystal is sheared.

(Courtesy P.M. Anderson)

Imperfections in Solids

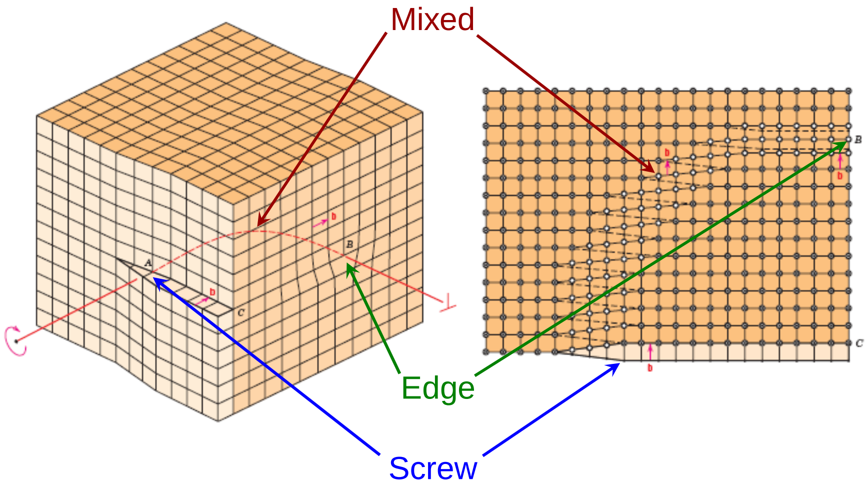
Screw Dislocation



(a) (b)

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

Edge, Screw, and Mixed Dislocations



Mixed

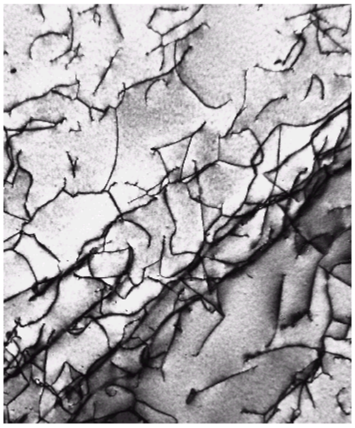
Edge

Screw

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

Imperfections in Solids

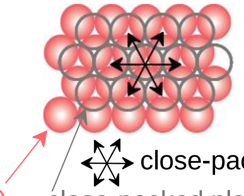
Dislocations are visible in electron micrographs



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

Dislocations & Crystal Structures

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



view onto two close-packed planes.

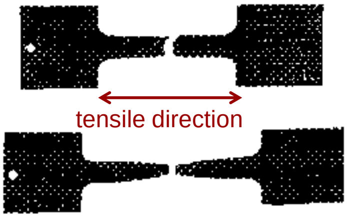
close-packed directions

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.

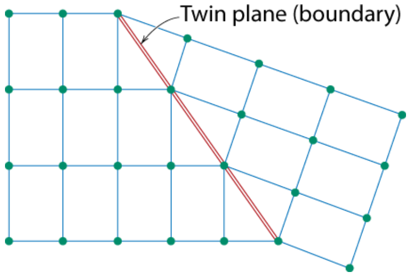


Mg (HCP)

Al (FCC)

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 7e.*

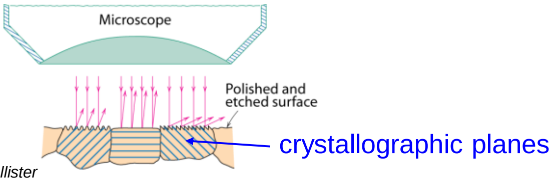
- Stacking faults
  - For FCC metals an error in ABCABC packing sequence
  - Ex: ABCABABC

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)

Optical Microscopy

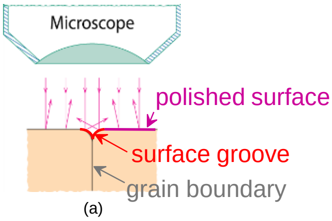
Grain boundaries...

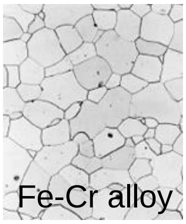
- are imperfections,
- are more susceptible to etching,
- may be revealed as dark lines,
- change in crystal orientation across boundary.

ASTM grain size number

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

number of grains/in^2 at 100x magnification





(b)

Adapted from Fig. 4.14(a) and (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].)

Optical Microscopy

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

Microscopy

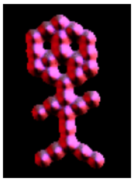
Optical resolution ca. 10^{-7} m = 0.1 μm = 100 nm

For higher resolution need higher frequency

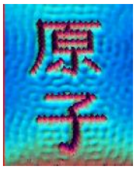
- X-Rays? Difficult to focus.
- Electrons
  - wavelengths ca. 3 pm (0.003 nm)
    - (Magnification - 1,000,000X)
  - Atomic resolution possible
  - Electron beam focused by magnetic lenses.

Scanning Tunneling Microscopy (STM)

- Atoms can be arranged and imaged!



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

- 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.)

ANNOUNCEMENTS

Reading:

Core Problems:

Self-help Problems: