Imperfections in solids + Metallography and Microstructure

Imperfections in Solids

There is no such thing as a perfect crystal.

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

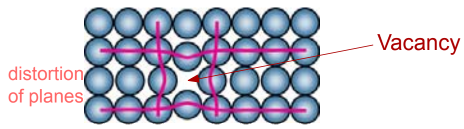
Many of the important properties of materials are due to the presence of imperfections.

Types of Imperfections

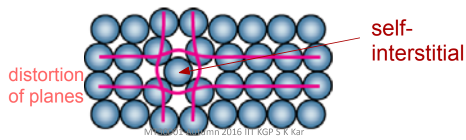
• Vacancy, Self interstitials • Impurity atoms ▪ Interstitial ▪ Substitutional	Point defects
• Dislocations	Line defects
• Grain Boundaries, Stacking Faults, Twin Boundaries, Anti Phase Boundaries	Area defects
• Pores, blow holes, Pin holes	Volume defects

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

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

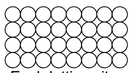
No. of potential defect sites.

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

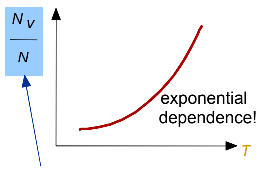
For most metals, the fraction of vacancies N_v/N *just below the melting temperature is on the order of* 10^4; *that is*, one lattice site out of 10,000 will be empty

Measuring Activation Energy

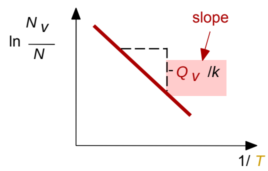
- We can get Q_v from an experiment.

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

- Measure this...
- Replot it...



defect concentration



Estimating Vacancy Concentration

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

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

Q_v = 0.9 eV/atom $\quad N_A$ = 6.02 x 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 x 10^{-5} eV/atom-K

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

- Answer:

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

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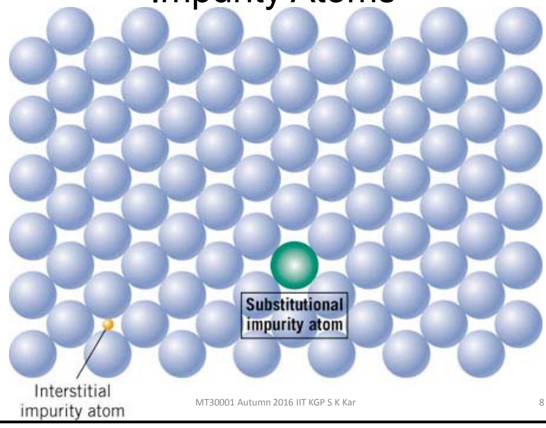
Impurity Atoms



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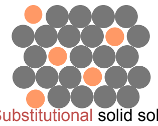
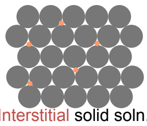
Point Defects in Alloys

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

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

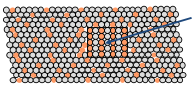


OR



Substitutional solid soln. (e.g., Cu in Ni) — Interstitial solid soln. (e.g., C in Fe)

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



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

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Substitutional Solid Solution

Conditions for substitutional solid solution (S.S.)

- 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

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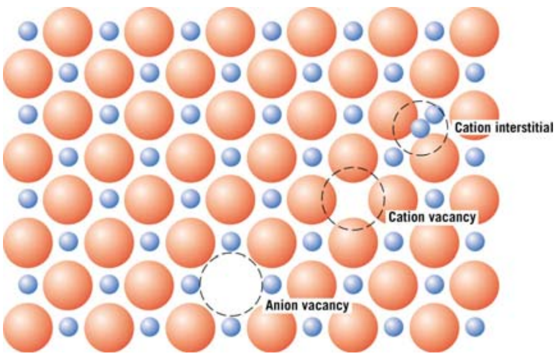
Defects in Ceramic Structures



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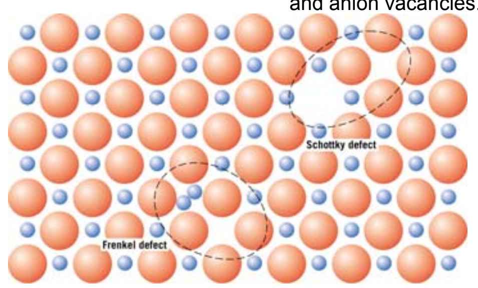
Defects in Ceramic Structures

- **Frenkel Defect**
  A cation is out of place.
- **Shottky Defect**
  A paired set of cation and anion vacancies.



- Equilibrium concentration of defects $\sim e^{-Q_D/2kT}$

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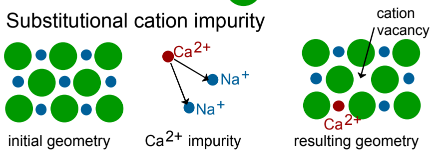
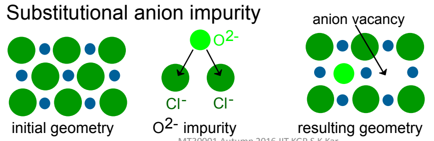
Impurities

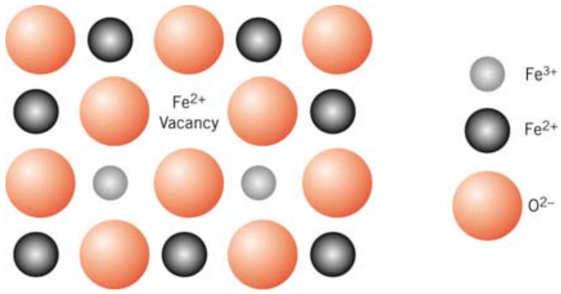
- Impurities must also satisfy charge balance = Electroneutrality
  - Ex: NaCl Na^{+} Cl^{-}
- Substitutional cation impurity



- Substitutional anion impurity

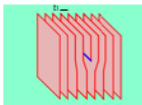


Non Stoichiometric compound



Line Defects (Dislocations)

Linear defects around which some of the atoms of the crystal lattice are misaligned



- Edge dislocation:
  - ➢Caused by the termination of a plane of atoms in the middle of a crystal.
  - ➢The adjacent planes are not straight, but instead bend around the edge of the terminating plane so that the crystal structure is perfectly ordered on either side.
- Screw dislocation:
  - ➢ More difficult to visualise
  - ➢ Comprises a structure in which a helical path is traced around the linear defect (dislocation line) by the planes of atoms in the crystal lattice

Burgers Vector

•The presence of dislocation results in lattice strain (distortion).

•The direction and magnitude of such distortion is expressed in terms of a Burgers vector (b).

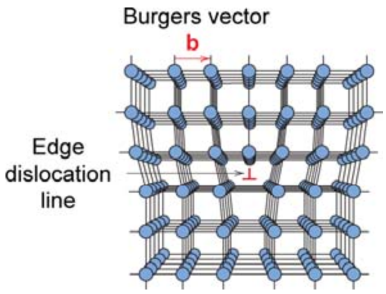
Edge dislocation:

- •Extra half-plane of atoms inserted in a crystal structure
- •**b ⊥ to dislocation line**

Screw dislocation:

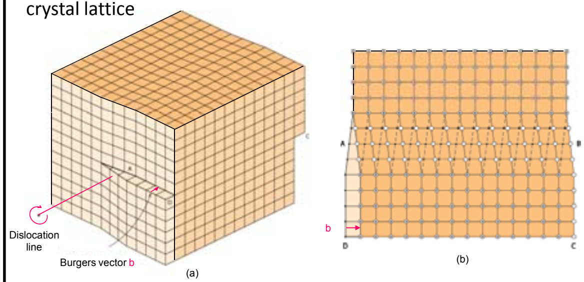
- •spiral planar ramp resulting from shear deformation
- •**b || to dislocation line**

Edge Dislocation

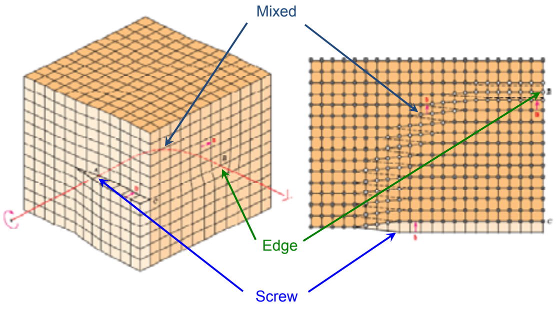


Screw Dislocation

Comprises a structure in which a helical path is traced around the linear defect (dislocation line) by the atomic planes of atoms in the crystal lattice



Edge, Screw, and Mixed Dislocations



Burgers Vector

- Even though a dislocation changes direction and nature within a crystal (e.g., from edge to mixed to screw), the Burgers vector will be the same at all points along its line.
- For example, all positions of the curved dislocation will have the Burgers vector shown.
- For metallic materials, the Burgers vector for a dislocation will point in a close-packed crystallographic direction and will be of magnitude equal to the interatomic spacing.

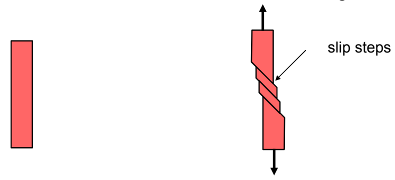
Dislocation motion – Ductility of material

- Dislocations can move if the atoms from one of the surrounding planes break their bonds and rebond with the atoms at the terminating edge.
- It is the presence of dislocations and their ability to readily move (and interact) under the influence of stresses induced by external loads that leads to the characteristic malleability of metallic materials.

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



Characterization of dislocations

Dislocations can be observed using transmission electron microscopy, field ion microscopy and atom probe techniques

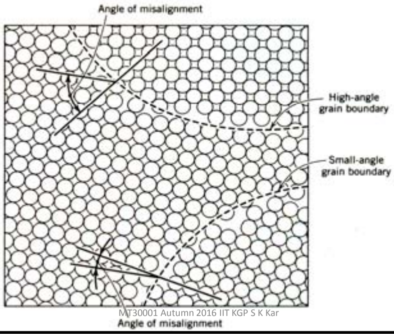
Dislocations are visible in electron micrographs

Planar Defects

- External Surface
- Grain Boundary
- Twin Boundary
- Phase Boundary
- Stacking Fault
- Domain Boundary
- Anti Phase Boundary

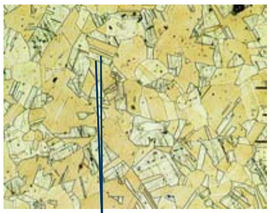
Grain Boundary

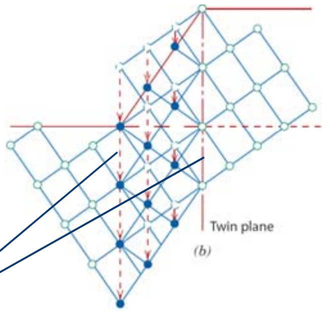
- Crystals of different orientations meet.
- A single-phase interface, with crystals on each side of the boundary being identical except in orientation.



Twin Boundary

Essentially a reflection of atom positions across the twin plane

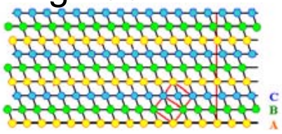


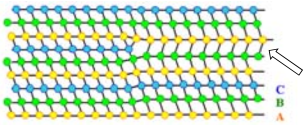


Twinned structure : Typical characteristics – always parallel lines are present

Stacking Fault

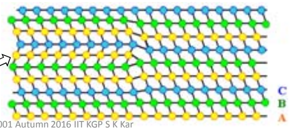
ABCABCABCA…





ABCA**BA**BCA…
"intrinsic stacking fault"
Removal of layer C

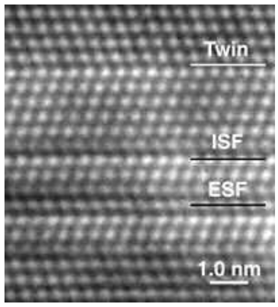
ABCA**BAC**ABCA…
"extrinsic stacking fault"
Insertion of layer A



Stacking Fault

HRTEM (high-resolution TEM) image shows the atomic structure of planar defects in thin-film silicon:

- a twin defect
- an intrinsic stacking fault (ISF)
- an extrinsic stacking fault (ESF—in which there is an intervening layer between two layers slightly shifted from each other)

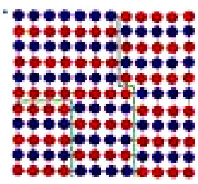


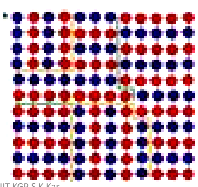
Anti Phase Boundary

occur in ordered alloys

The crystallographic direction remains the same

If the ordering is usually ABABABAB, an anti phase boundary takes the form of ABA**BB**ABA.





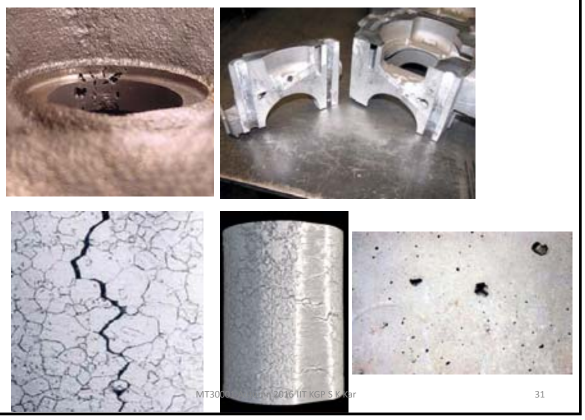
Bulk defects

Voids are small regions where there are no atoms, and can be thought of as clusters of vacancies.

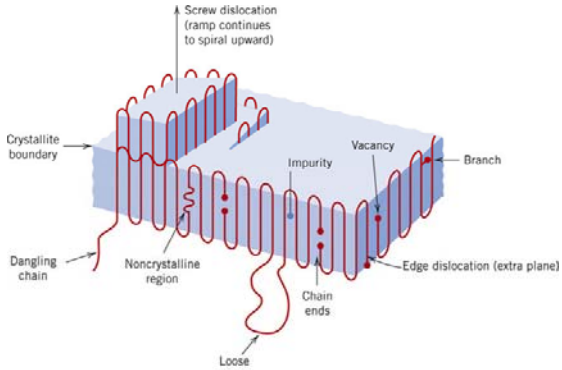
Impurities can cluster together to form small regions of a different phase. These are often called precipitates.

Cracks, other phases are also fall in this category.

Volume defects

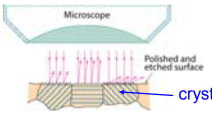


Imperfections in Polymers



Optical Microscopy

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



Micrograph of brass (a Cu-Zn alloy)

0.75mm

Optical Microscopy

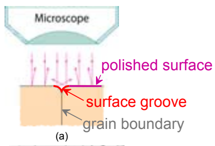
Grain boundaries...

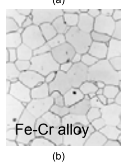
- are imperfections,
- are more susceptible to etching,
- may be revealed as dark lines,
- change in crystal orientation across boundary.

ASTM grain size number

$N = 2^{n-1}$

number of grains/in^2 at 100x magnification





Microscopy

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

For higher resolution need higher frequency

- Electrons
  - Wavelengths ca. 3 pm (0.003 nm)
  - Atomic resolution possible
  - Electron beam focused by magnetic lenses.