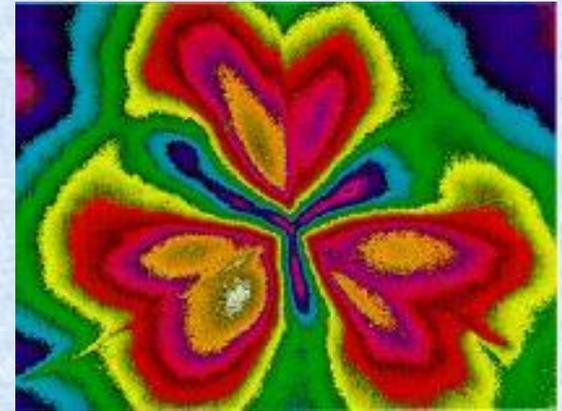


CHAPTER 4: *IMPERFECTIONS IN SOLIDS*

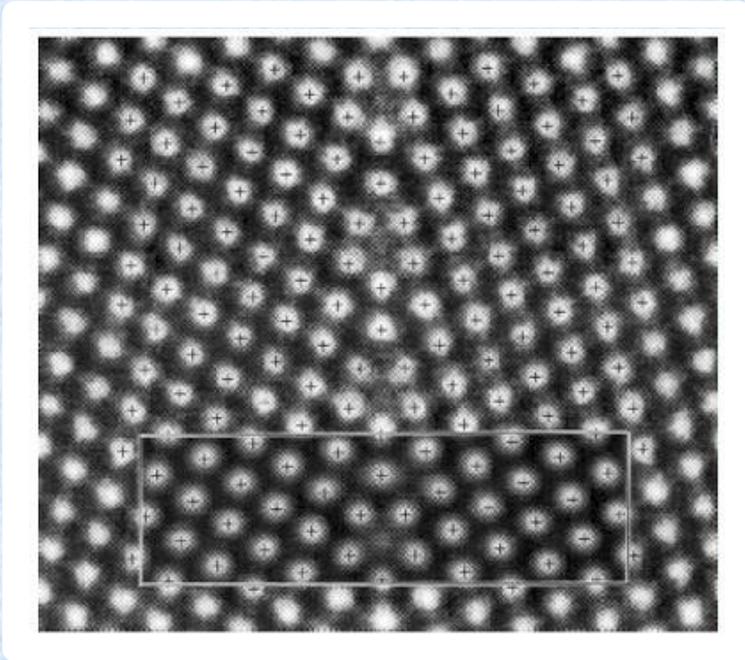


ISSUES TO ADDRESS...

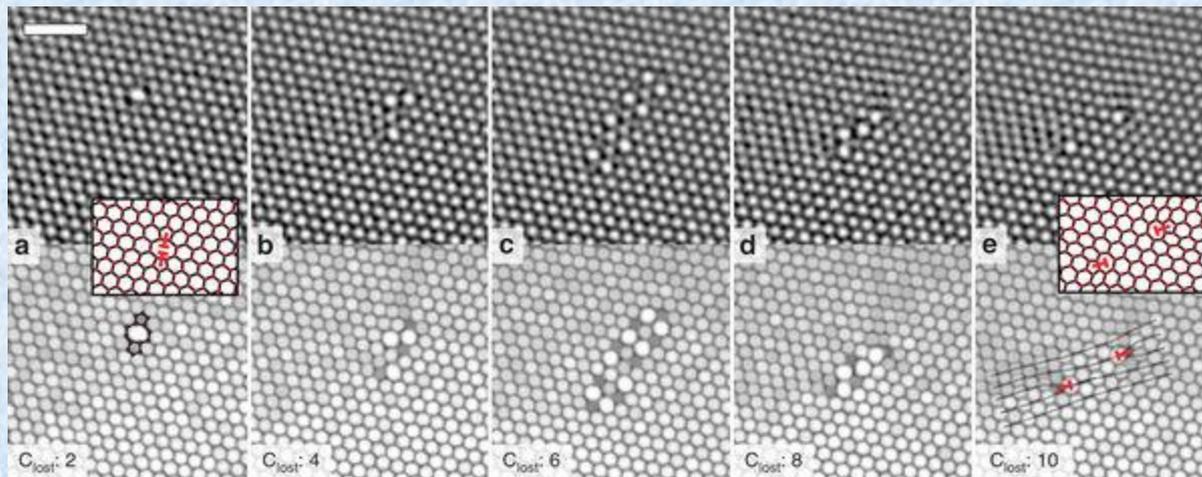
- What *types of defects* arise in solids?
- Can the number and type of defects be varied and *controlled* ?
- How do defects *affect material properties*?
- Are all defects *undesirable*?



REAL CRYSTALS



- **Real crystals** are never perfect: there are **always defects!**
- **Controlling** the defects is one of **the main** goal of materials science and engineering!



Imperfections in Solids

- The **properties** of materials are profoundly **influenced** by the presence of **imperfections**.
- It is important to have knowledge about the **types of imperfections** that exist and the roles they play in **affecting** the behavior of materials.

Types of Imperfections

Point defects

- Vacancy atoms
- Self-Interstitial atoms
- Impurities: Substitutional and Interstitial atoms

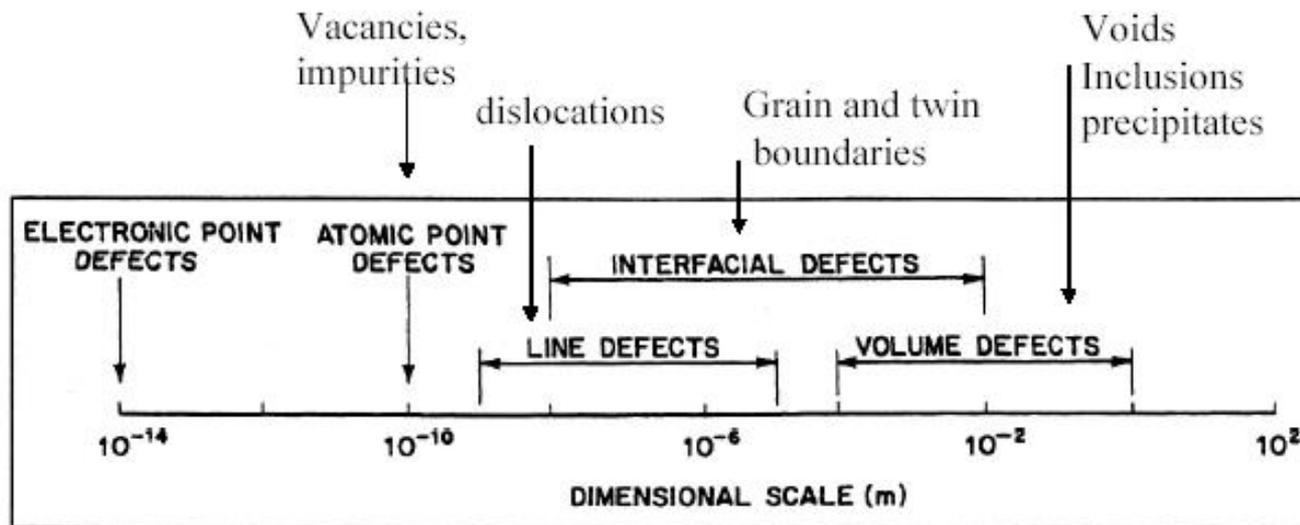
Line defects

- Dislocations

Area defects

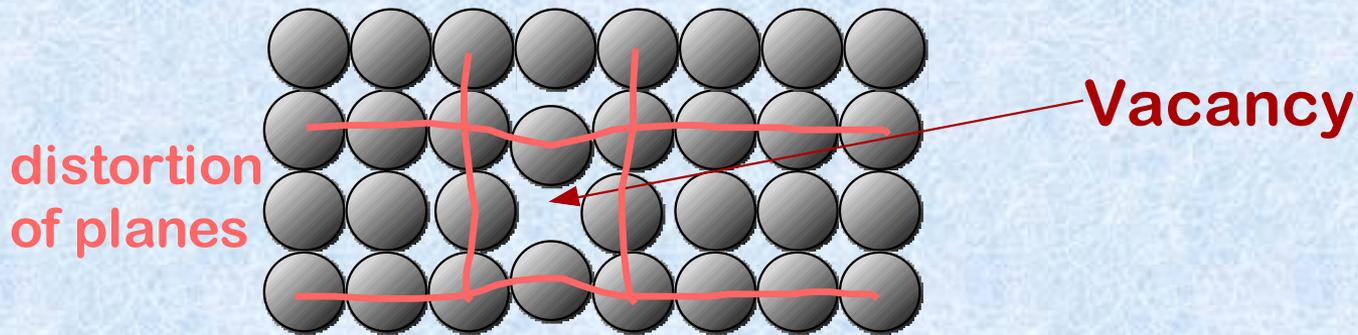
- Grain Boundaries

Dimensional Ranges of Different Classes of Defects

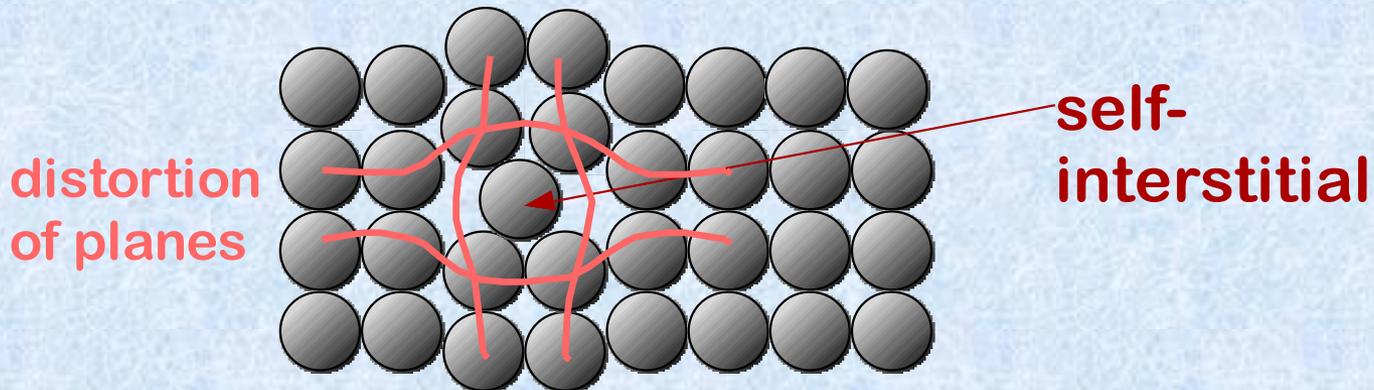


Point Defects (I)

Vacancies: vacant atomic sites in a structure.

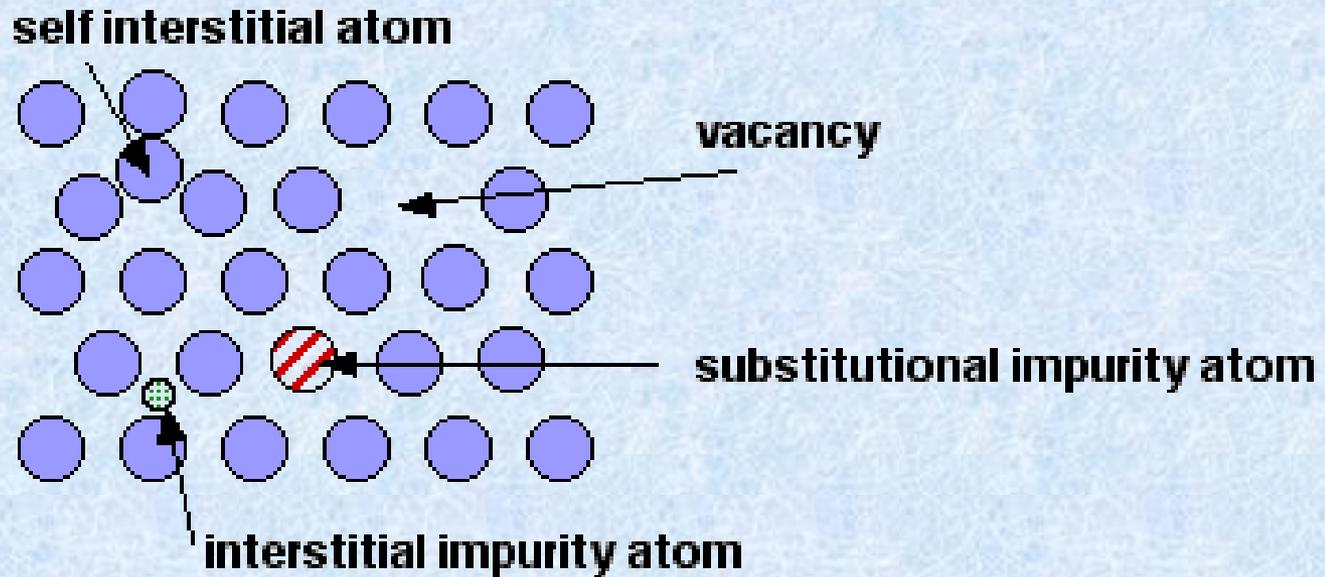


Self-Interstitials: "extra" atoms positioned between atomic sites



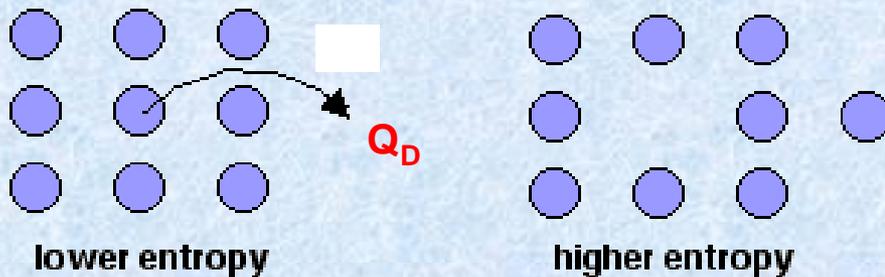
Point Defects (II)

- Substitutional impurity – impurity atom in lattice
- Interstitial impurity – impurity atom not in regular lattice site



- in principle you can eliminate all of these except vacancies
- vacancies arise from thermodynamics (entropy)

Equilibrium Concentration: Vacancies



Each lattice site
is a potential
vacancy site

$$N = \rho \times (N_A/A) \times V$$

where: ρ - density; A – atomic mass
 V – volume and N_A – Avogadro number
 (6.02 x 10²³ atom/mol)

$$\frac{N_D}{N} = \exp\left(\frac{-Q_D}{kT}\right)$$

where:

N - is number of sites

N_D - is number of defects

Q_D – is activation energy

T – is a temperature

k – Boltzmann's constant

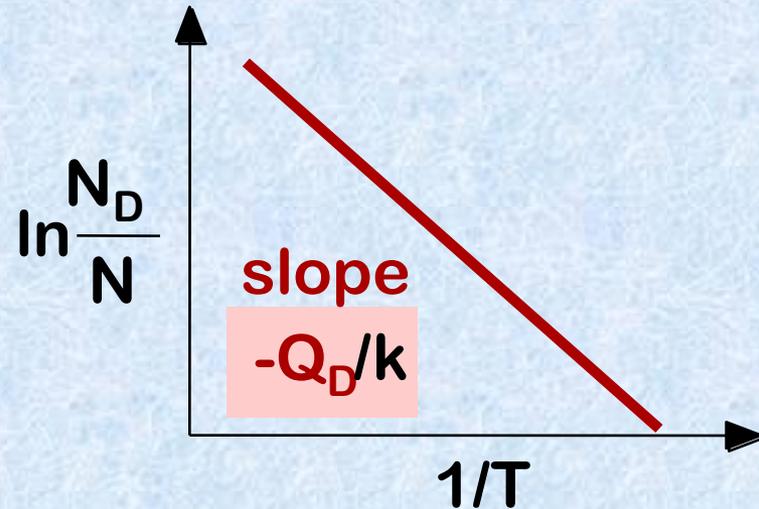
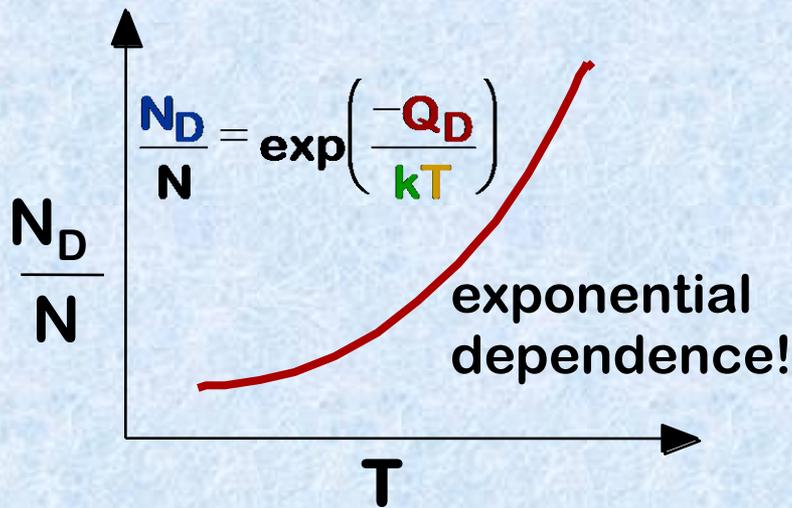
1.38 x 10⁻²³ J/atom K

8.62 x 10⁻⁵ eV/atom-K

1 eV = 1.602 · 10⁻¹⁹ J

Measuring Activation Energy

- We can get Q_D from an experiment
- Plot data in the so-called Arrhenius form:



- typically Q_D is $\sim 1 \text{ eV} = 1.602 \cdot 10^{-19} \text{ J}$
- at room temperature, N_D/N is $\sim 10^{-17}$

Equilibrium Concentration of Vacancies

- Find the equilibrium number of vacancies in 1m^3 of Cu at $1000\text{ }^\circ\text{C}$.

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

$$A_{\text{Cu}} = 63.5\text{g/mol}$$

$$Q_{\text{D}} = 0.9\text{eV/atom}$$

$$N_{\text{A}} = 6.02 \times 10^{23}\text{ atoms/mole}$$

For 1 m^3 , $N = \rho \cdot N_{\text{A}}/A_{\text{Cu}} \cdot 1\text{m}^3 = 8 \cdot 10^{28}$ sites

$$\frac{N_{\text{D}}}{N} = \exp\left(\frac{-Q_{\text{D}}}{kT}\right) = 2.7 \cdot 10^{-4}$$

0.9eV/atom
 1273K
 $8.62 \times 10^{-5}\text{ eV/atom-K}$

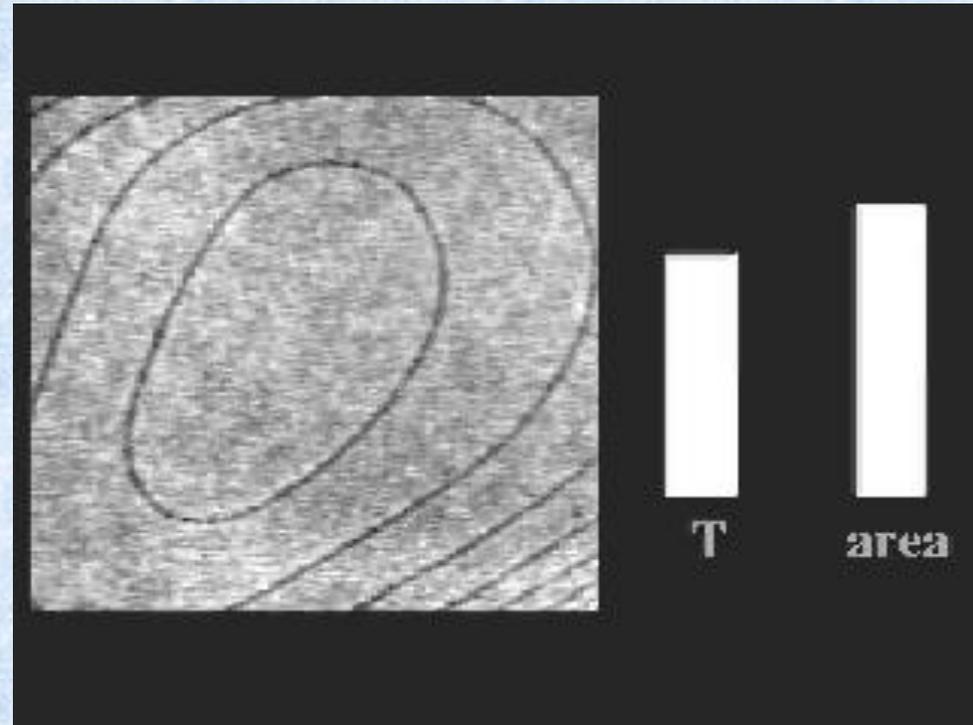
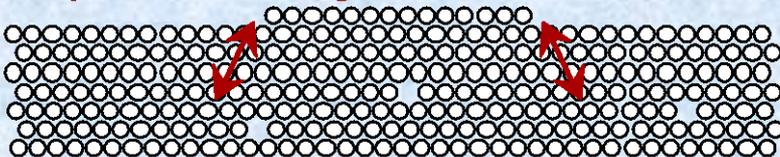
- Answer:

$$N_{\text{D}} = 2.7 \cdot 10^{-4} \cdot 8.0 \times 10^{28}\text{ sites} = 2.2 \times 10^{25}\text{ vacancies}$$

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 equilibrium vacancy concentration increases via atom motion from the crystal to the surface, where they join the island.

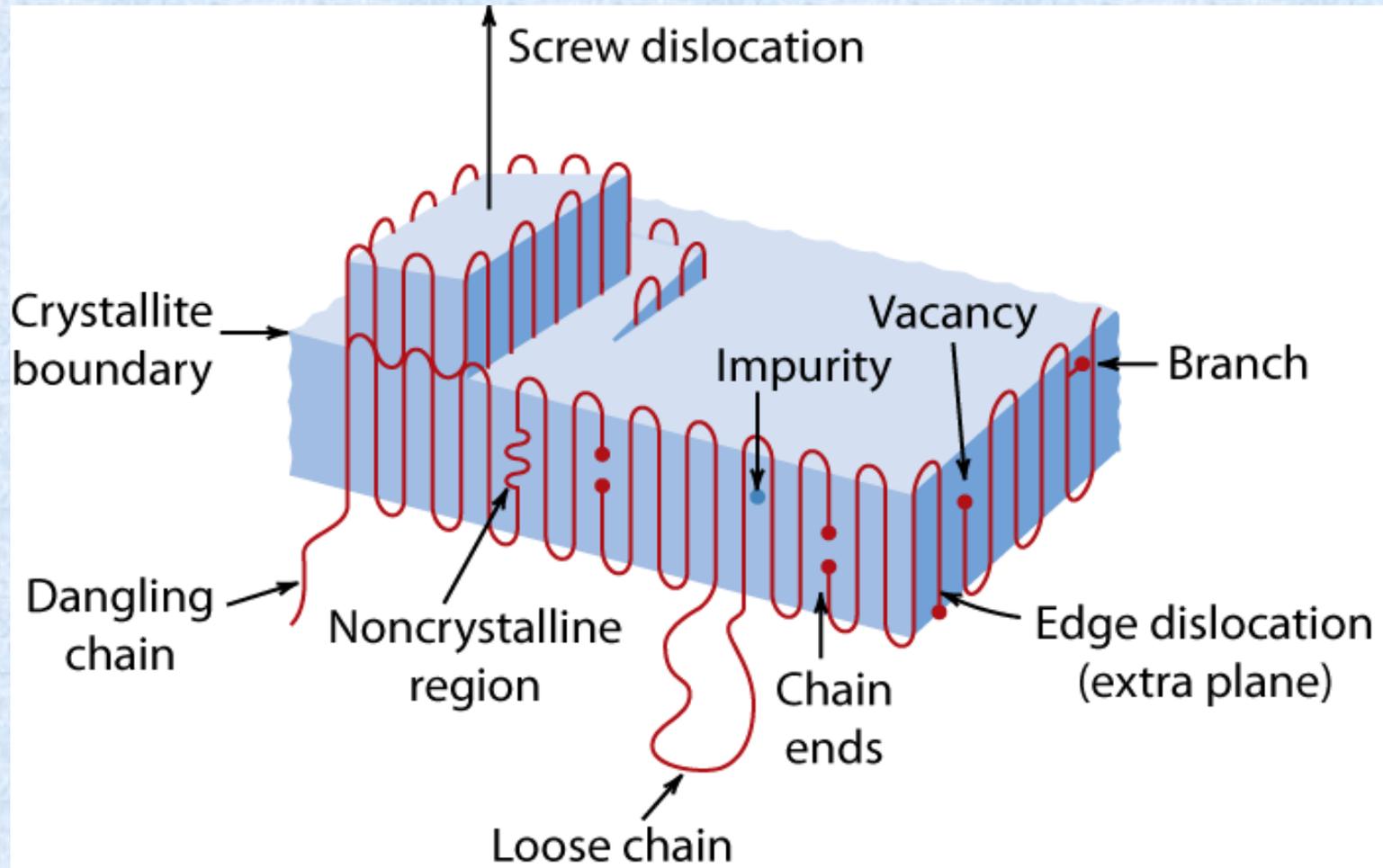
Island grows/shrinks to maintain equil. vacancy conc. in the bulk.



(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.

Point Defects in Polymers

- Defects due in part to chain packing errors and impurities such as chain ends and side chains



Methods of producing point defects

❑ Growth and synthesis

Impurities may be added to the material during synthesis

❑ Thermal & thermochemical treatments and other stimuli

- Heating to high temperature and quench
- Heating in reactive atmosphere
- Heating in vacuum → e.g. in oxides it may lead to loss of oxygen
- Etc.

❑ Plastic Deformation

❑ Ion implantation and irradiation

- Electron irradiation (typically $>1\text{MeV}$)
 - Direct momentum transfer or during relaxation of electronic excitations)
- Ion beam implantation (As, B etc.)
- Neutron irradiation

Alloys

- An **alloy** is a combination, either in solution or compound, of two or more elements, at least one of which is a metal.
- An alloy with two components is called a binary alloy; one with three is a ternary alloy; one with four is a quaternary alloy.
- The result of alloying is a metallic substance with properties different from those of its components.

Example: **Steel** is a metallic alloy whose major constituent is iron. One classical definition is that steels are iron-carbon alloys with up to 2.1% carbon. With the increased carbon, steel is harder and has a much higher tensile strength than iron, but is also more brittle.

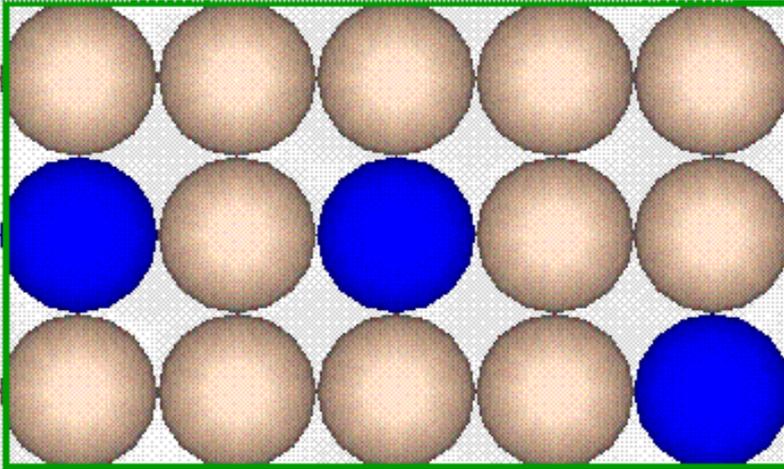
Solid Solutions (I)

The extent to which the components of an alloy are miscible depends on the interaction between the atoms:

- If strong mutual attraction occurs, a single crystal of a ***different phases*** can form, such as in intermetallic compounds
- If there is little difference between like and unlike bonds, then a ***solid solution*** can occur, over a wide range of elemental compositions
- If the species do not tend to bond to each other, then ***separate phases*** will form with limited or zero miscibility (***pseudo-alloys***).

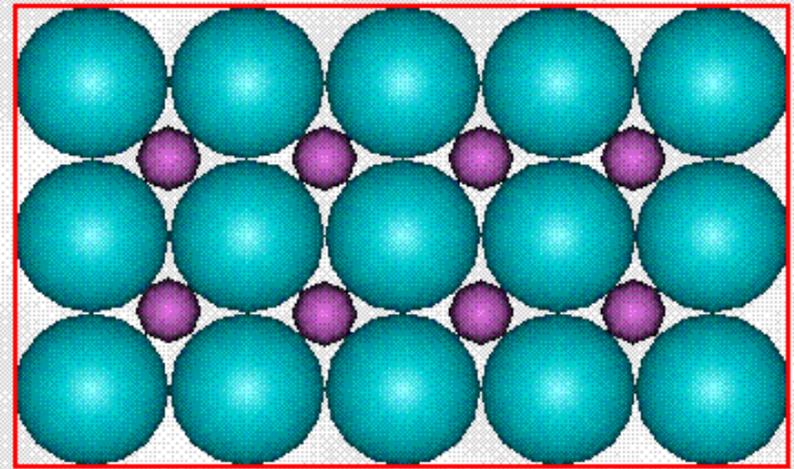
Types of Solid Solutions

SUBSTITUTIONAL SOLID SOLUTION



The name – substitutional- of this solid solution tells you exactly what happens as atoms of the **parent metal** are replaced or substituted by atoms of the **alloying metal**.

Interstitial Solid Solution



In interstitial solid solutions the atoms of the parent or **solvent metal** are bigger than the atoms of the alloying or **solute metal**. In this case, the smaller atoms fit into interstices i.e. spaces between the larger atoms.

In both cases the overall atomic structure is virtually unchanged.

Range of Solubility in Substitutional Solid Solutions

Substitutional Solid Solutions can

- exist over a *limited composition range* – **limited solubility**;
- exist over the whole composition range – **full solubility**.

HUME ROTHERY RULES: basic conditions for appreciable solubility

1. Atomic Sizes: should not differ by more than 14%;
2. Crystal structures: same for “pure” metals;
3. Electronegativity: The atoms should have similar electronegativity, or compounds will form;
4. Valences: If (1) -(3) are favorable, then the metal of lower valence will dissolve more in crystal structure of the higher valence metal than vice versa.

Note: Not all alloys systems that fit these rules will form appreciable solid solutions

Example I

- **Cu-Ni Alloys**

Rule 1: $r_{\text{Cu}} = 0.128 \text{ nm}$ and $r_{\text{Ni}} = 0.125 \text{ nm}$.

$$\Delta R\% = 2.3\%$$

favorable ✓

Rule 2: Ni and Cu have the FCC crystal structure.

favorable ✓

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

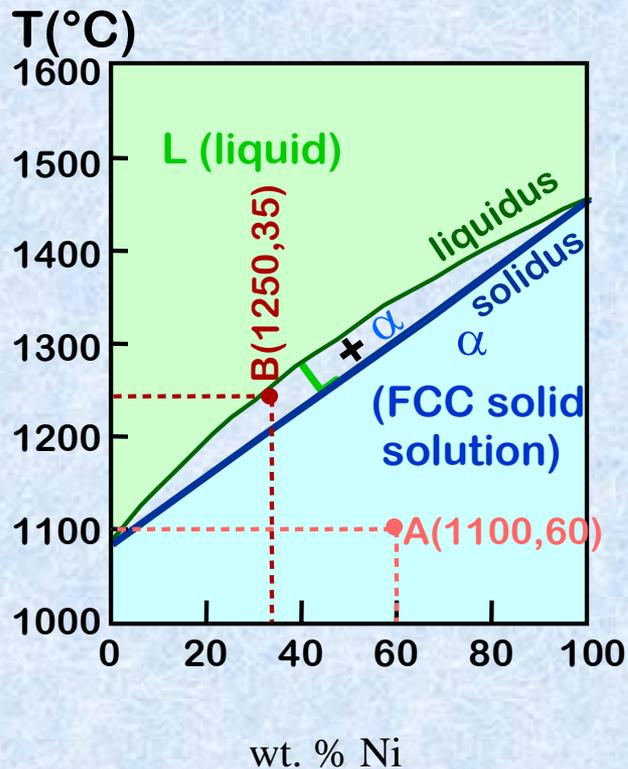
favorable ✓

Rule 4: Valency of Ni and Cu are both +2.

favorable ✓

Expect Ni and Cu forms S.S. over wide composition range.

Cu-Ni Binary System



- Both metals are completely soluble in each other. The α phase is a substitutional solid solution.
- This occurs because **both** the Cu and Ni form **FCC structures**, and have **close**:
 - atomic radii (1.28 and 1.25 Å),
 - electronegativity (1.9 and 1.8)
 - valence (+2).
- Cu and Ni show very different physical properties in their pure states, and the α phase provides a continuous change between the extremes.

Example II

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, $\Delta E\% = -5.2\%$

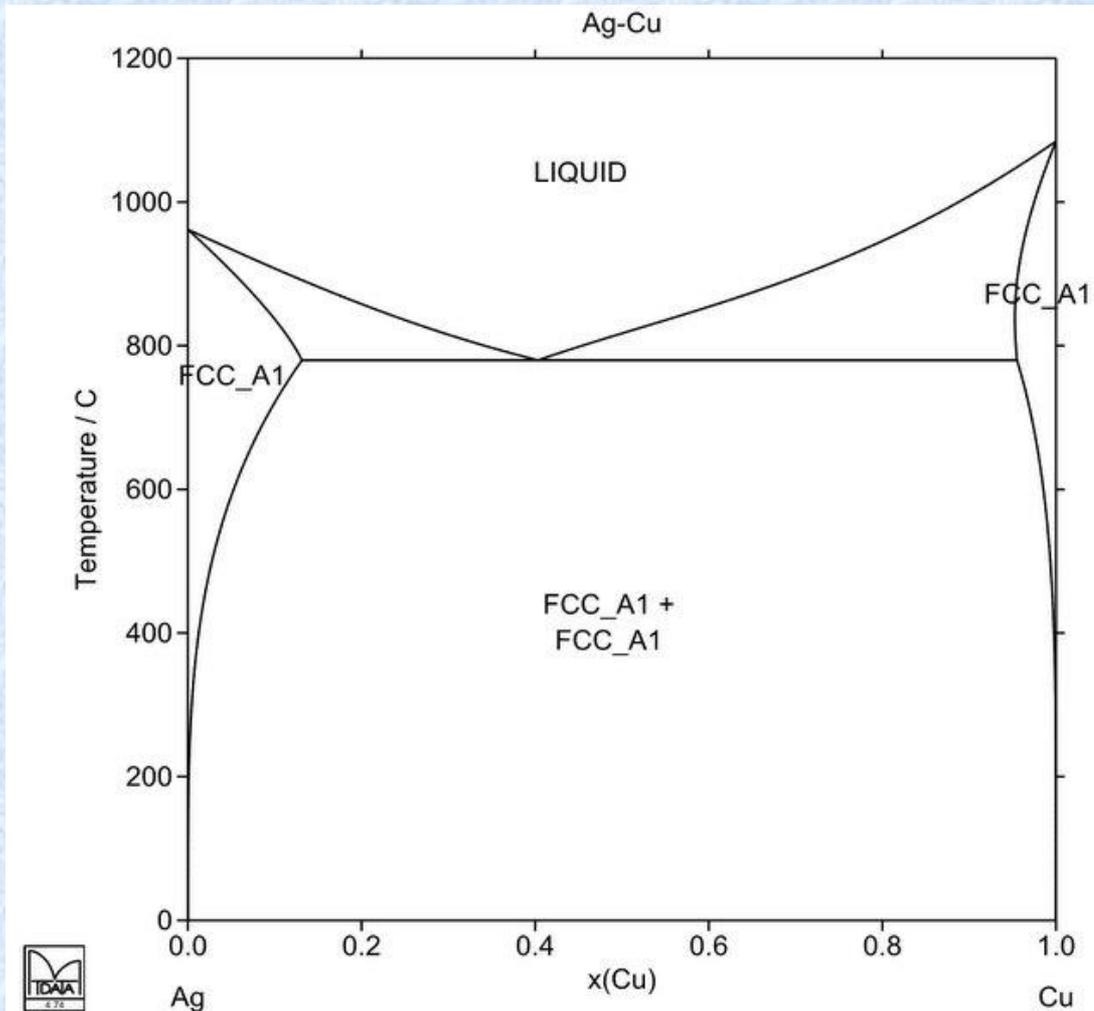
favorable ✓

Rule 4: Valency of Cu is +2 and Ag is +1.

NOT favorable

Expect Ag and Cu have limited solubility.

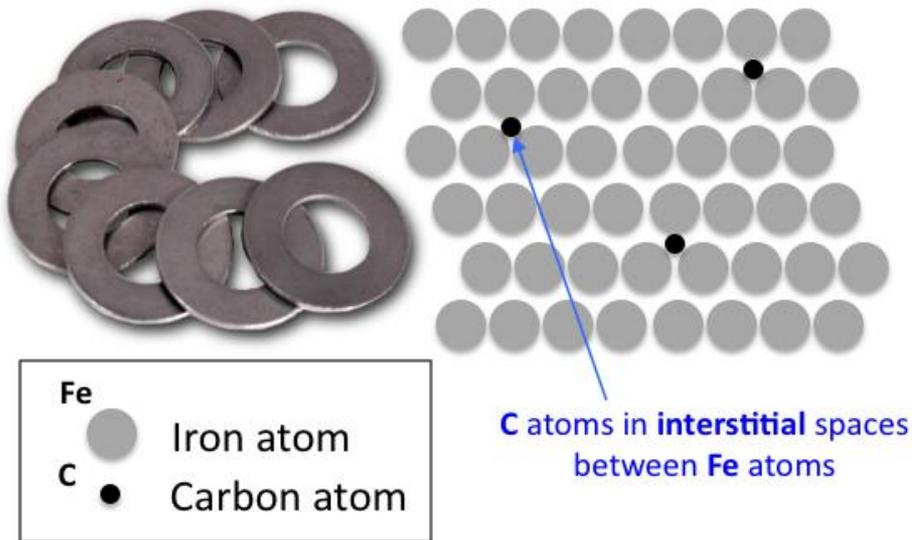
Cu-Ag Binary System



- In fact, the Cu-Ag phase diagram shows that solubility of only ~8 wt.% Ag can be achieved at high T in the Cu-rich alloy

Interstitial Solid Solutions: Example

Steel: An iron-carbon alloy



- Alloying with smaller atoms (C, N)
- Small atoms fill in interstitial spaces
- These atoms deform crystal lattice and introduce internal stress

Steel is an interstitial
iron-carbon alloy

Iron:

BCC and FCC

atomic radii:

BCC - 1.24 Å

FCC - 1.29 Å

valence +2 or +3

Carbon:

Hex. Cubic

atomic radii:

0.17 Å

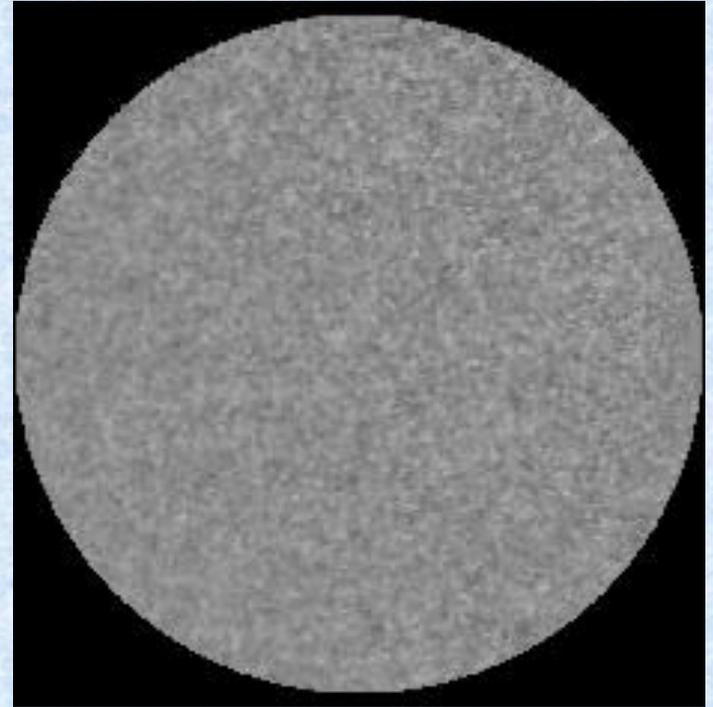
valence +4

The high temperature form of iron (austenite, FCC) can dissolve a max. of ~0.2 wt.% carbon at 1148°C.

The lower temperature form (ferrite, BCC) can only dissolve a max. of 0.02 % at 727°C

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.



Reprinted with permission from: A.K. Schmid, N.C. Bartelt, and R.Q. Hwang, "Alloying at Surfaces by the Migration of Reactive Two-Dimensional Islands", *Science*, Vol. 290, No. 5496, pp. 1561-64 (2000). Field of view is 1.5 μm and the temperature is 290K.

TYPES OF IMPERFECTIONS

- Vacancy atoms
- Interstitial atoms
- Substitutional atoms

Point defects

- **Dislocations**

Line defects

- Grain Boundaries

Planar Defects

Strength of a Material

- Based on the bond strength most materials should be much stronger than they are
- From Chapter 2 we know that the strength for an ionic bond should be about 1 GPa
- More typical strength is 200 MPa
- Why?
- **Materials must not usually fail by breaking bonds!!**

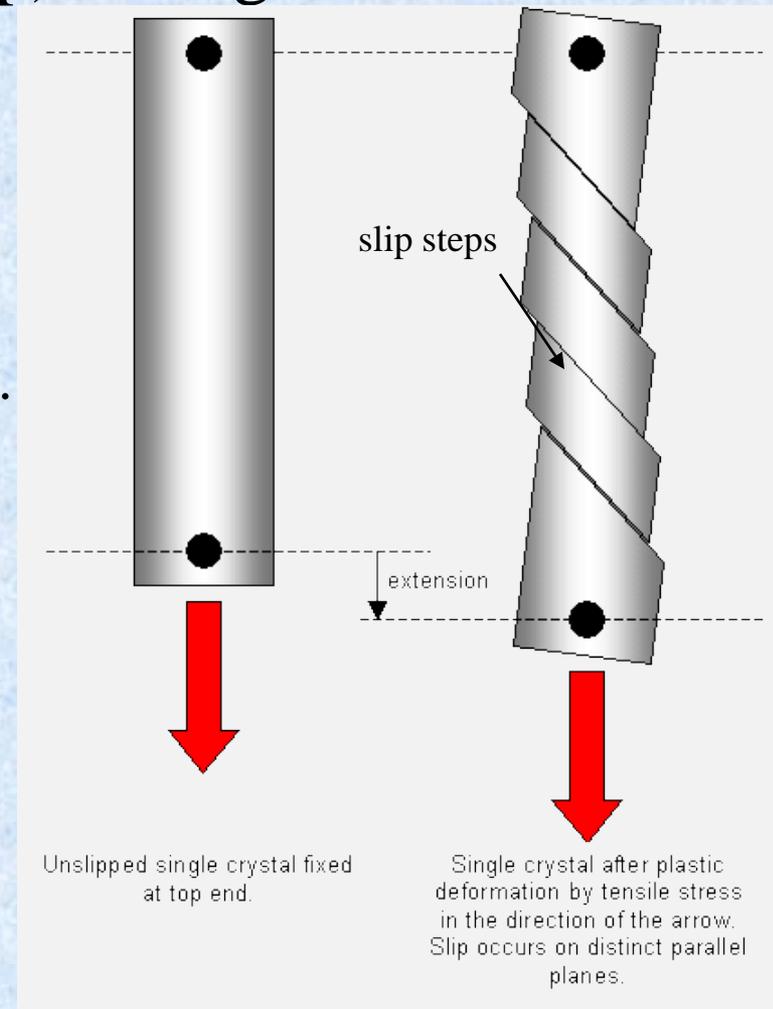
Line Defects

- Deformation of ductile materials occurs when a **line defect** (dislocation) moves (slip) through the material

Dislocations:

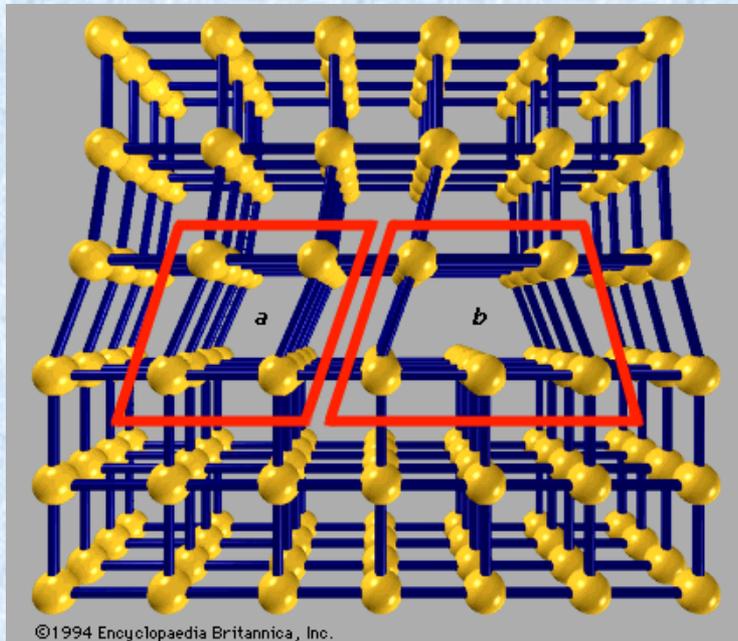
- are line defects;
- **slip between crystal planes** result when dislocations move;
- produce **permanent (plastic) deformation**.

Schematic of dislocation slip



Dislocations

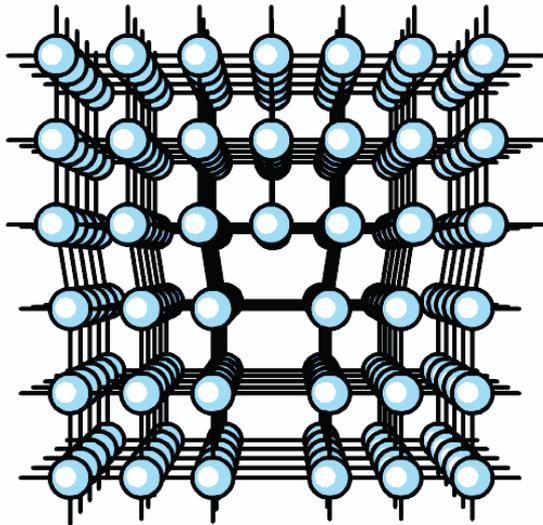
- are linear defects, lead to the **atom misalignment**
- cause slip between crystal plane when they move
- produce permanent (plastic) deformation.



- Dislocation Types:
 - *Edge dislocation*
 - *Crew dislocation*
 - *Mixed dislocation*

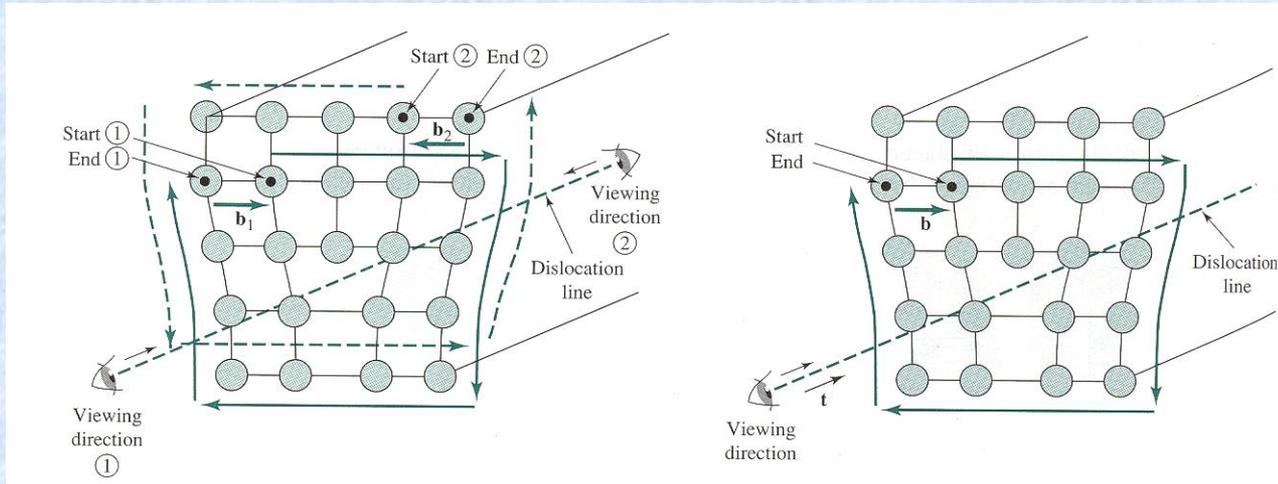
EDGE DISLOCATION

Edge dislocation centers around the *edge dislocation line* that is defined along **the end of the extra half-plane of atoms**



- *Distortion* to the lattice decreases with distance away from dislocation line;
- *Burgers* vector, **\mathbf{b}** , defines the magnitude and direction of the deformation;
- For edge dislocation **\mathbf{b}** and *dislocation line* are *perpendicular*

Burger Vector

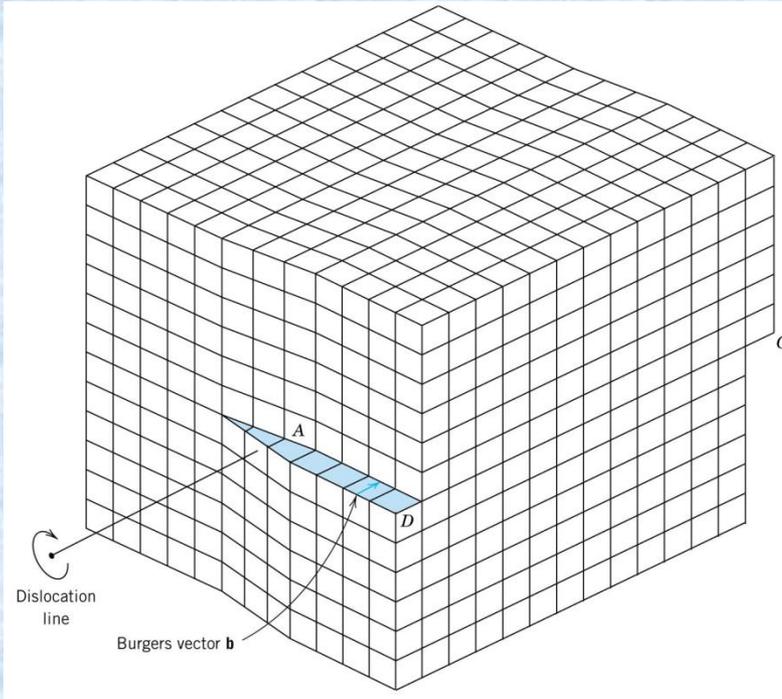


A Burger depends
on the viewing direction

The choice of positive
viewing direction:
"clockwise" Burgers circuit

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

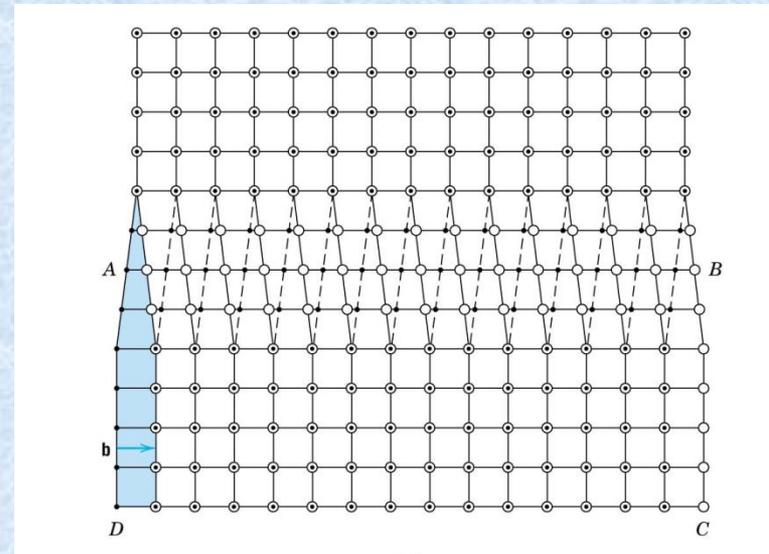
SCREW DISLOCATION



Harder to visualize than edge dislocations

- Open circles upper half atoms
- Solid circles lower half atoms
- Connecting “looks **like a screw**”

- Screw dislocation is a ramped step in crystal planes
- **Burgers vector** which defines the direction of the atoms displacement for a screw dislocation **is parallel** to the line of the dislocation

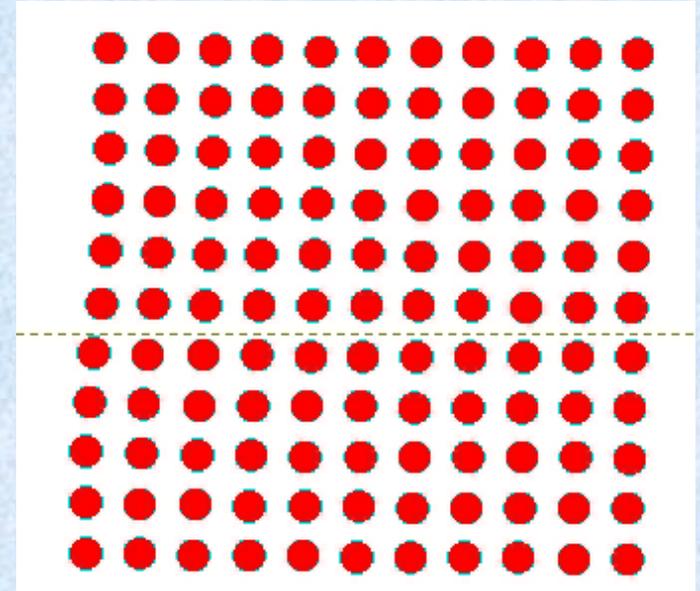


Deformation

- When a shear force is applied to a material, the dislocations move
- Real materials have lots of dislocations, therefore the strength of the material depends on the force required to make the dislocation move, not the bonding energy

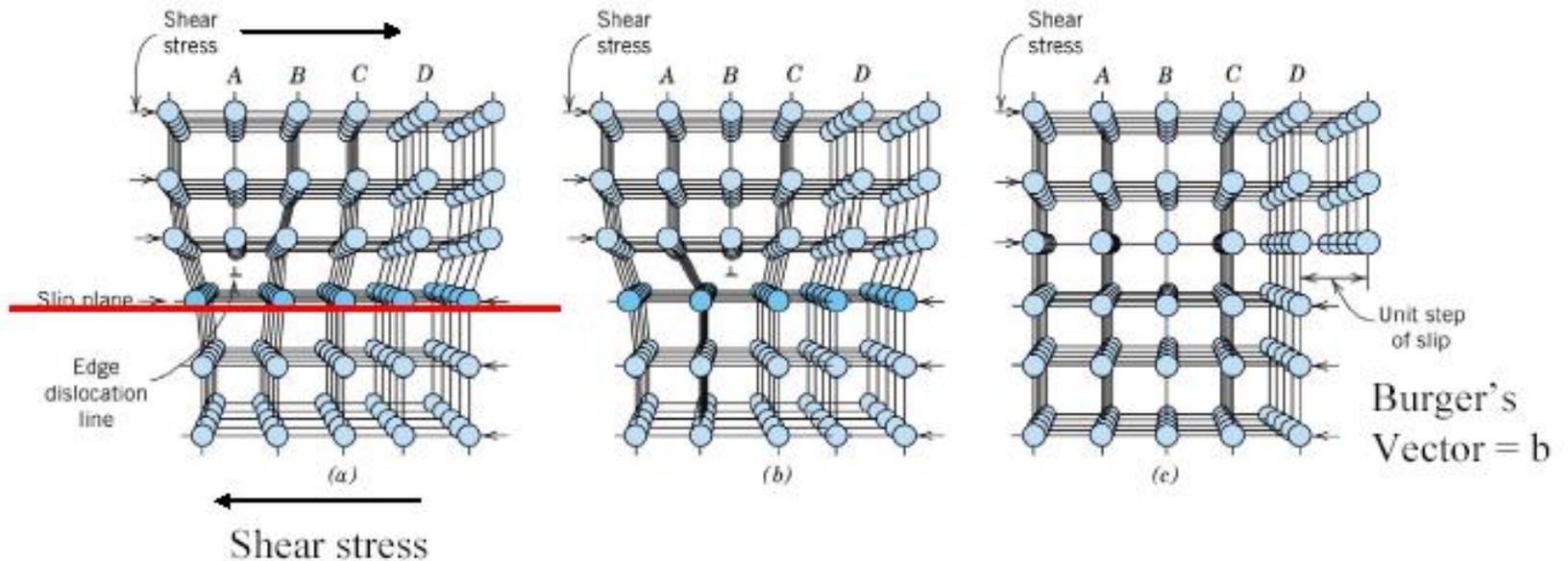
Motion of Edge Dislocation

- Dislocation motion requires **the successive bumping (slip) of a half plane of atoms.**
 - **Bonds across the slipping planes are broken and remade in succession.**
- The (plastic) permanent deformation of most crystalline materials is by dislocation movement.
 - Most contain some dislocations that were introduced during **solidification, plastic deformations, and rapid cooling (thermal stresses).**
 - To deform plastically means to slide atomic planes past each other.

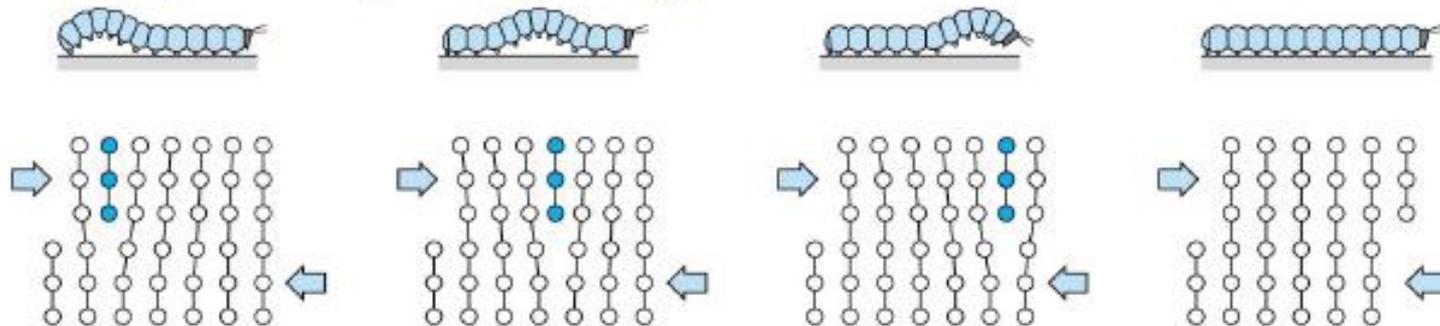


Atomic view of edge dislocation motion from left to right as a crystal is sheared.

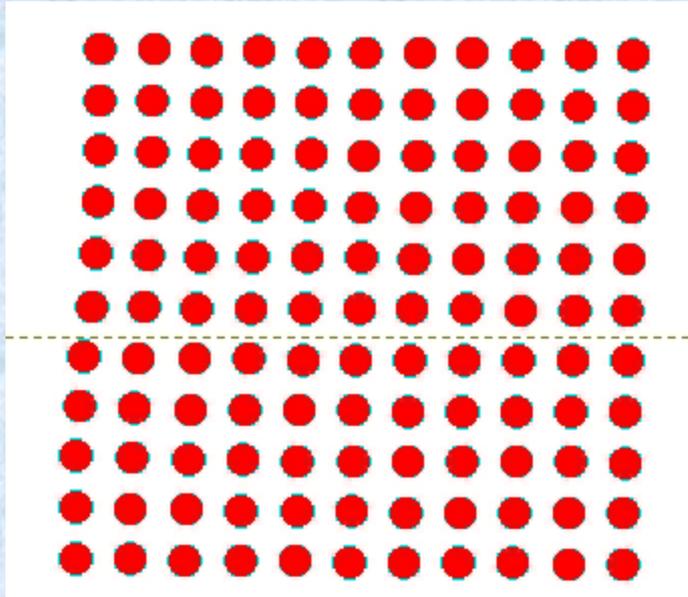
Edge Dislocation: Plastic Deformation



The caterpillar or rug-moving analogy



Slip: Crystallographic Requirements

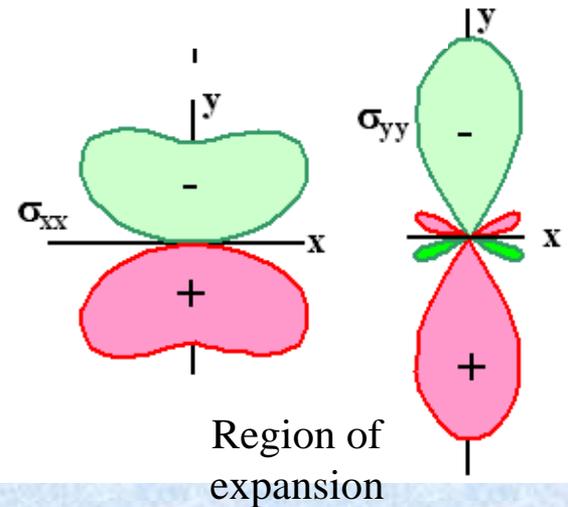
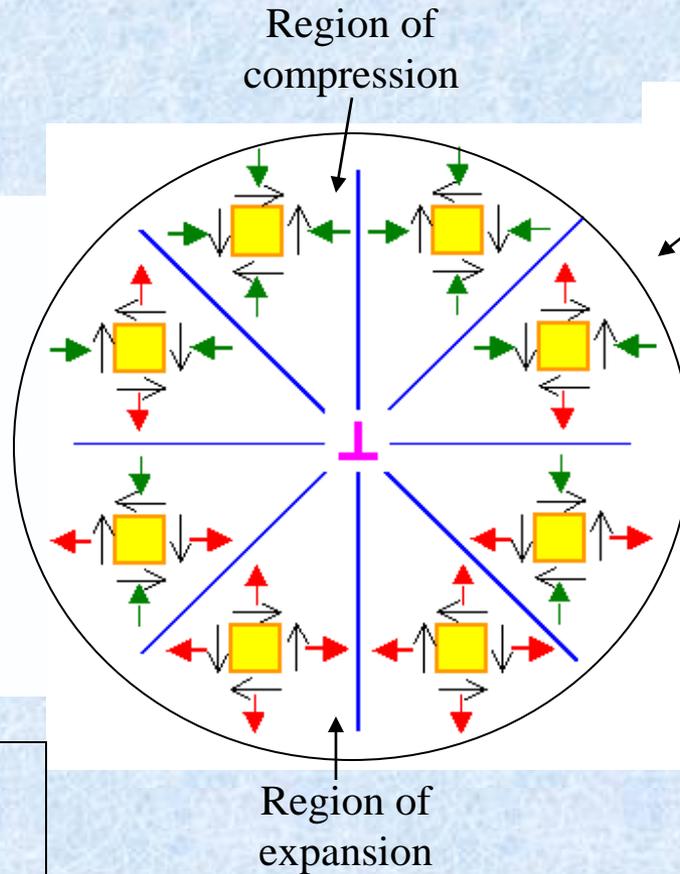
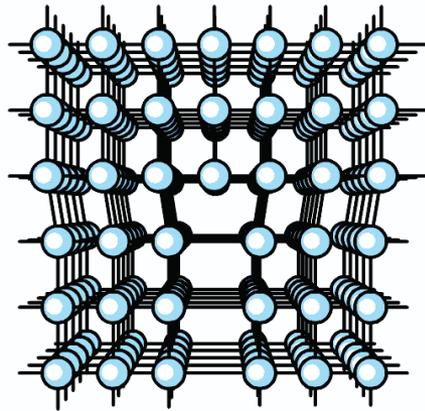


- Burger vector for unit dislocations **MUST** join crystallographically equivalent positions in the lattice
- The motion of the dislocation **MUST transport** atoms from one equilibrium position to another

Thus the most favorable Burgers vectors is the shortest vectors that connect equivalent lattice positions

In the simple crystal structures the Burgers Vectors are in the ***closed –packed directions!!!***

Slip: Energetic Considerations



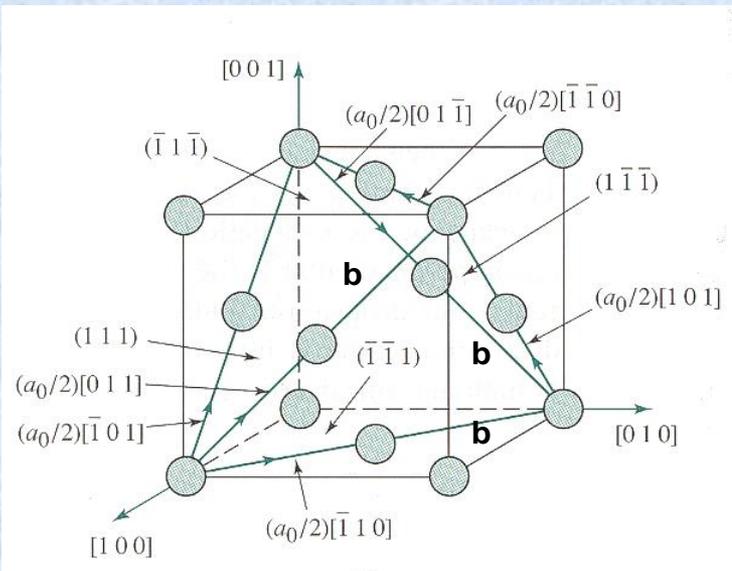
$$E_{\text{dist}} \sim 1/b^2$$

Thus energy associated with dislocation is a minimum
for the *shortest* Burger Vectors

What is a slip plane?

- When dislocations move slip occurs
 - Direction of movement – same as the Burgers vector
- Slip is easiest on ***close packed planes***
- Slip is easiest in the ***close packed direction***

Burgers Vectors and Slip Systems: FCC Crystal Structure

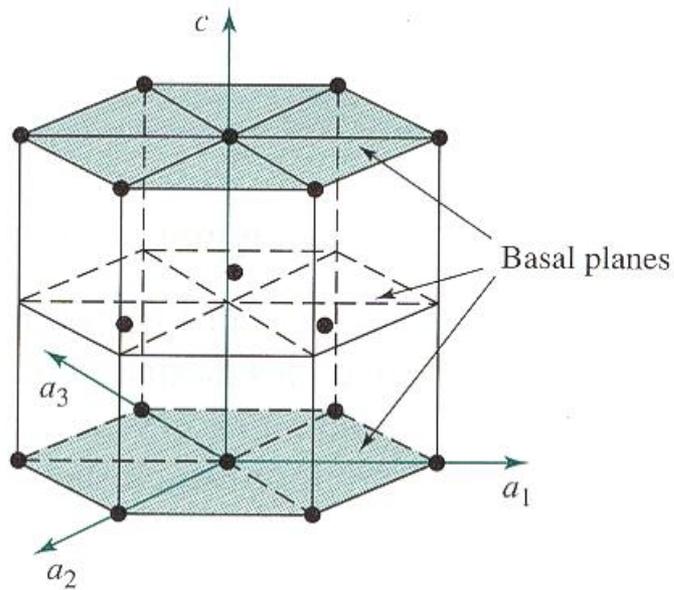


- {111} planes are the closed-packed and hence the slip planes;
- The shortest vector joining equivalent lattice positions – one half of any face diagonal
- These vectors belong to <110> family of directions

- The combination of a slip direction and slip plane = slip system
- There are four nonparallel {111} planes
- Each contains three nonparallel directions <110>
- Thus 12 slip systems in FCC are collectively represented as {111}<110>

Burgers Vectors and Slip Systems

HCP Crystal Structure

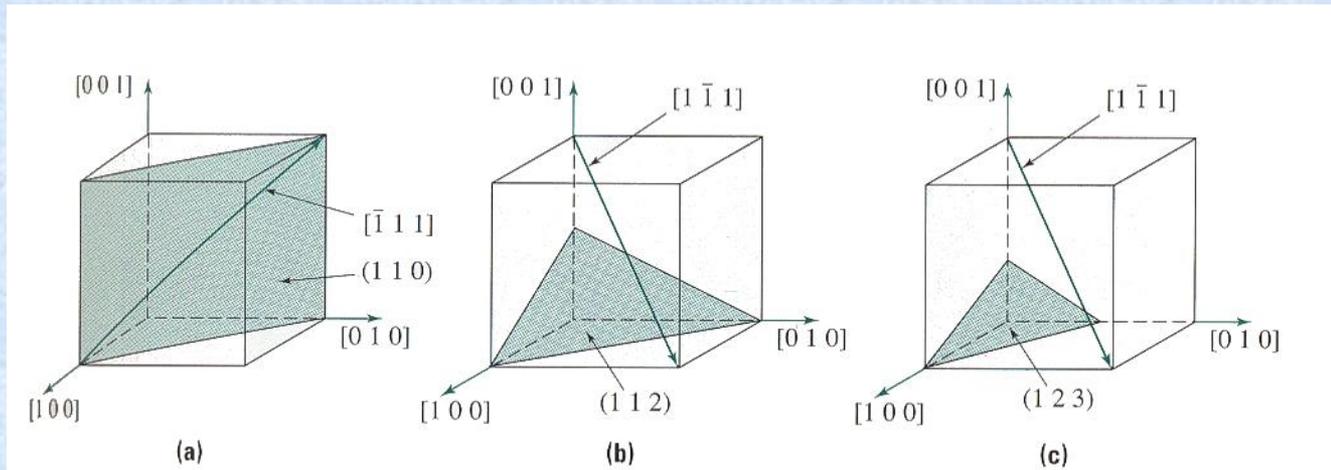


- Basal or (0001) planes represent one set of parallel closed-packed slip planes
- This one set contains three slip directions $\langle 11\bar{2}0 \rangle$ family in the “a” directions – *basal slip*
- Thus there are three not intersected slip systems in the HCP structure

Burgers Vectors and Slip Systems BCC Crystal Structure

There are no closed-packed planes in BCC structure!!

The planes of highest atomic density frequently observed to be a *slip planes*

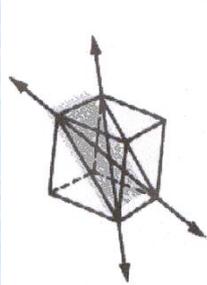
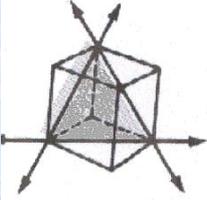
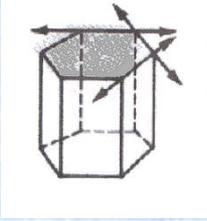


A member of the
 $\{110\}\langle 111\rangle$ system

A member of the
 $\{112\}\langle 111\rangle$ system

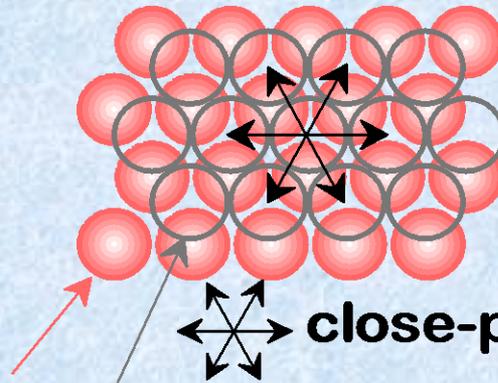
A member of the
 $\{123\}\langle 111\rangle$ system

Major Slip Systems in the Common Metal Structures

Crystal Structure	Slip Plane	Slip Directions	Number Of Slip Systems	Unit Cell Geometry	Examples
BCC	$\{110\}$ $\{211\}$ $\{321\}$	$\langle 111 \rangle$ $\langle 111 \rangle$ $\langle 111 \rangle$	$6 \times 2 = 12$ $6 \times 2 = 12$ $6 \times 4 = 24$		α -Fe, Mo, W
FCC	$\{111\}$	$\langle 110 \rangle$	$3 \times 4 = 12$		Al, Cu, γ -Fe, Ni
HCP	Basal	a	$1 \times 3 = 3$		α -Ti, Mg, Zn, Cd

DISLOCATIONS & CRYSTAL STRUCTURE

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



view onto two close-packed planes.

close-packed plane (bottom) **close-packed plane (top)**

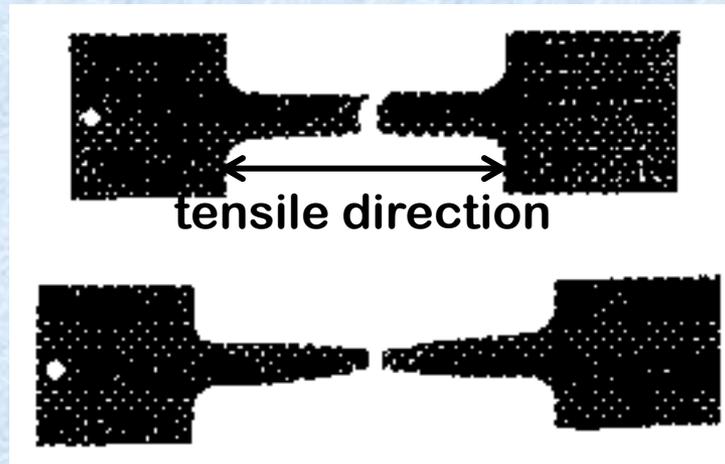
- **Comparison among crystal structures:**

FCC: many close-packed planes/directions;

HCP: only one plane, 3 directions;

BCC: none

- Results of tensile testing.



Mg (HCP)

Al (FCC)

Dislocations and Mechanical Properties

- The strength of a material with no dislocations is 20-100 times greater than the strength of a material with a high dislocation density.
- So, materials with no dislocations may be very strong, but they cannot be deformed.
- The dislocations weaken a material, but make plastic deformation possible.

Characteristics of Dislocations

- During plastic deformation, the number of dislocations increase dramatically to densities of 10^{10} mm^{-2} .
- Grain boundaries, internal defects and surface irregularities serve as formation sites for dislocations during deformation.

TYPES OF IMPERFECTIONS

- Vacancy atoms
- Interstitial atoms
- Substitutional atoms

Point defects

- Dislocations

Line defects

- **Free Surfaces in Crystal**
- **Grain Boundaries**
- **Stacking Faults**
- **Low-Angle Tilt Boundary**
- **A Twin**

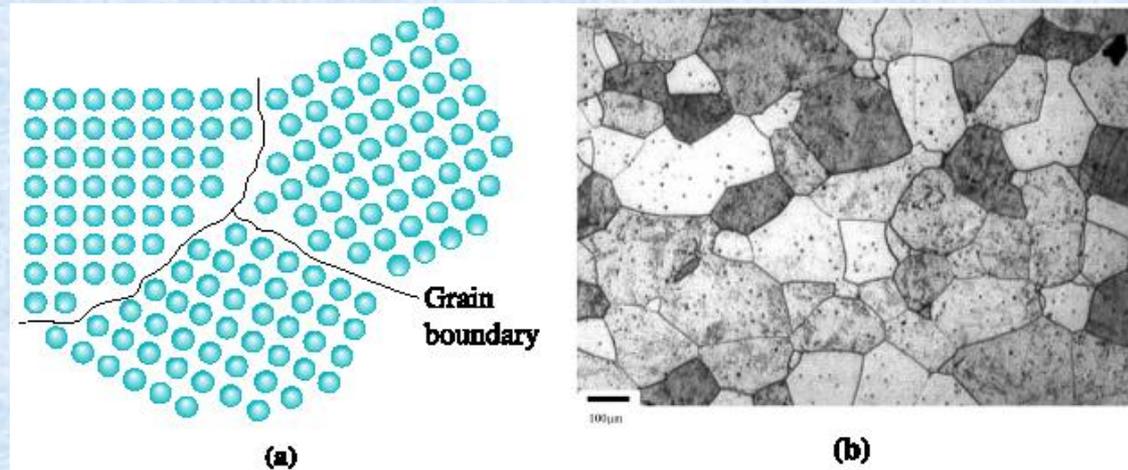
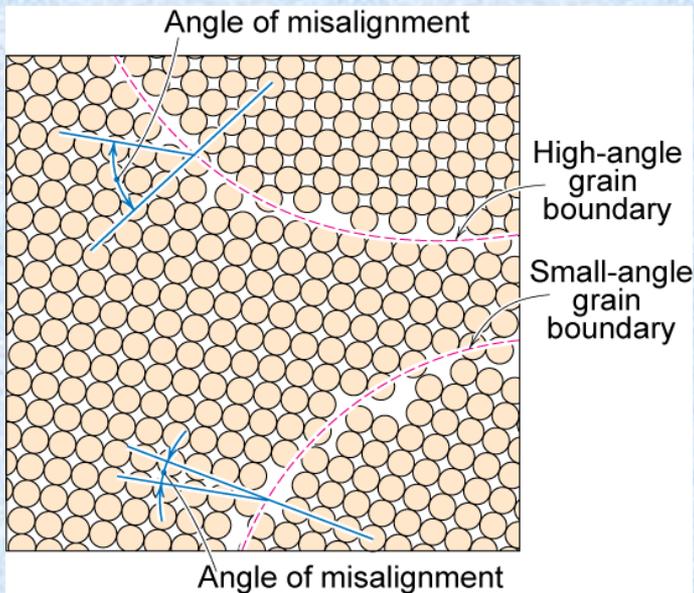
Planar Defects

Grain Boundaries

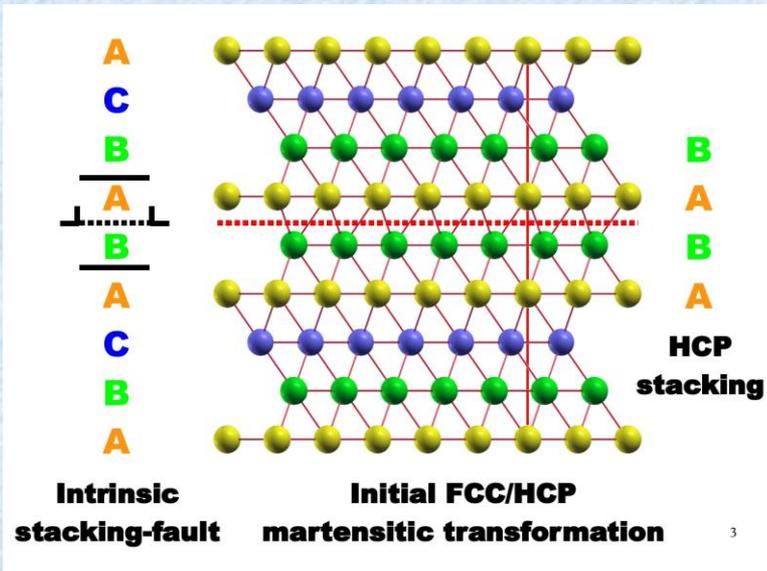
Grain boundaries:

- boundaries between crystals.
- have a change in crystal orientation across them.
- impede dislocation motion.
- produced by the solidification process, for example.

Schematic



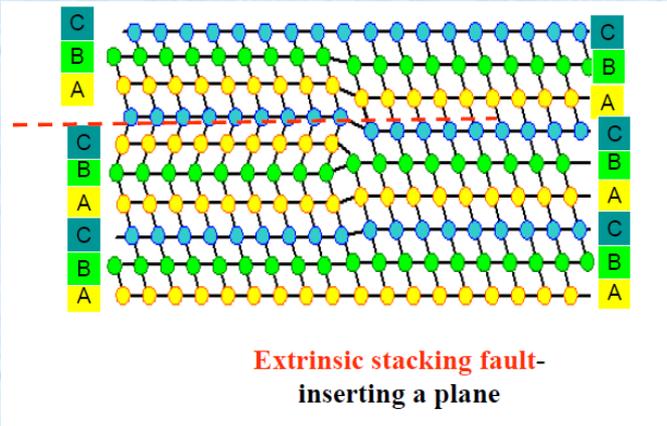
Stacking Faults



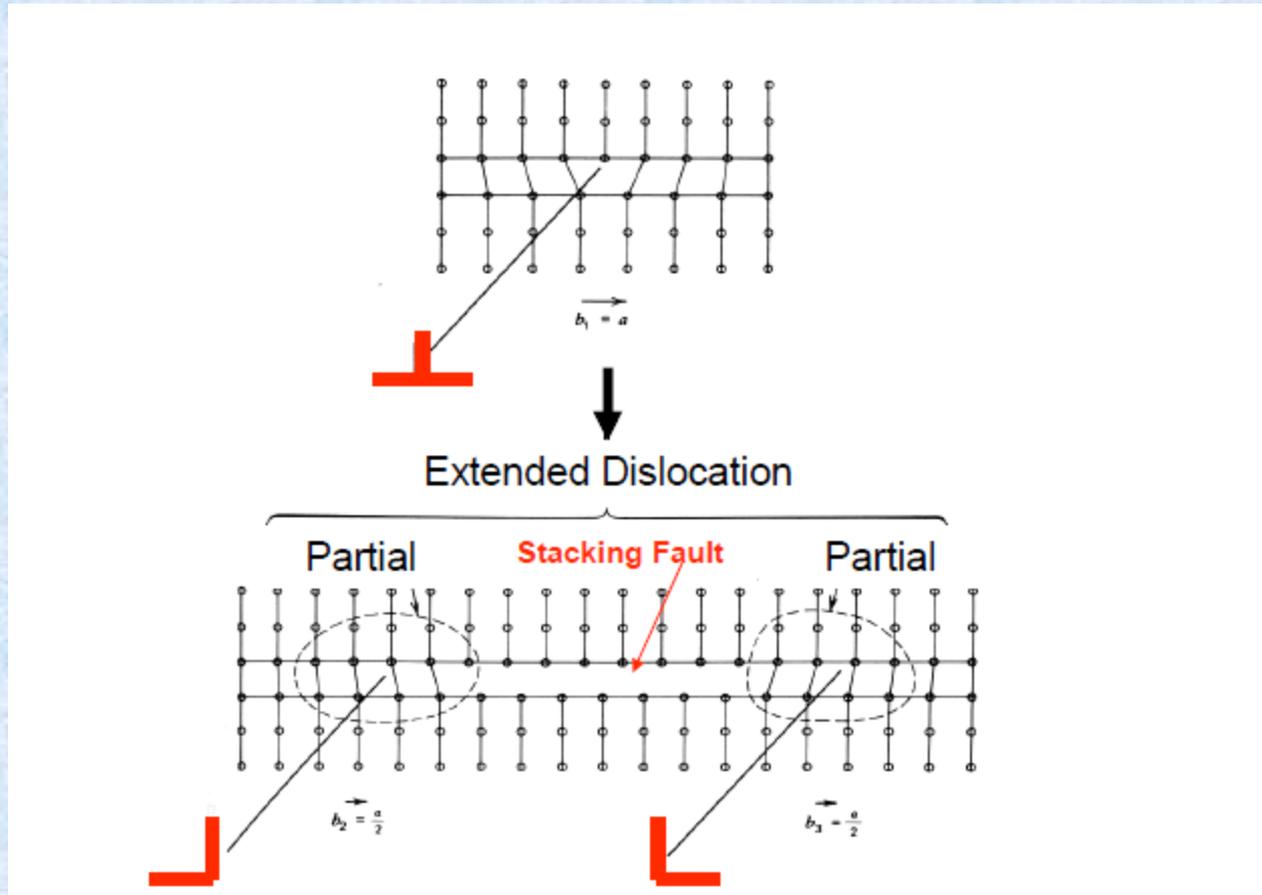
A Stacking Fault (SF) is a an **error in the staking sequence** of planes in the crystal. Common examples are **intrinsic** and **extrinsic** SF on $\{111\}$ in FCC metals.

In the first case, the lattice “collapse” along $[111]$ by $d_{111} = a/\sqrt{3} = |a/3 \cdot [111]|$, leaving two overlapping layers AB, AB of HCP stacking. Produced by quenching.

In the second case, is produced by adding a new layer: two non overlapping layers of HCP stacking. Produced by irradiation.



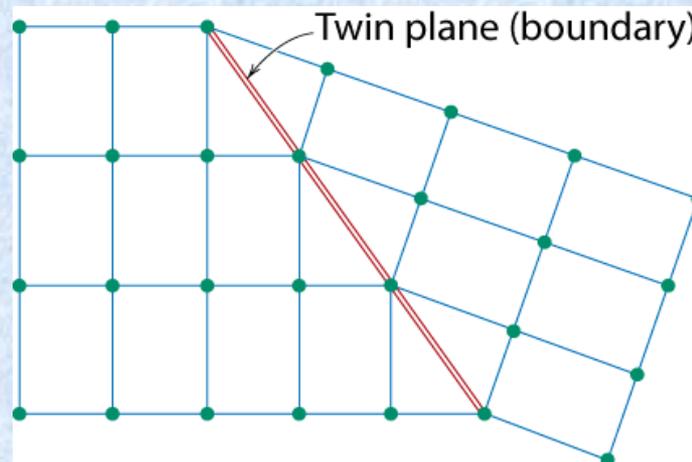
Dislocations & Stacking Faults



“Perfect” dislocation in FCC structure have $\mathbf{b} = \mathbf{a}/2 \cdot [110]$, a centering translation, which connects like atoms. However, the “perfect” $a/2[110]$ dislocation can “split” into two Shockley partial dislocations with $\mathbf{b} = \mathbf{a}/6 \cdot [211]$ separated by ribbon of stacking faults of width d . The width of d is large for the alloys with low stacking fault energy γ (J/cm²): $d \sim 1/\gamma!!$

Planar Defects in Solids - Twinning

- A shear force that causes atomic displacements such that the atoms on one side of a plane (twin boundary) mirror the atoms on the other side. A reflection of atom positions across the **twin plane**.
- Displacement magnitude in the twin region is proportional to the atom's distance from the twin plane.
- Takes place along defined planes and directions depending upon the system.
 - Ex: BCC twinning occurs on the $(112)[111]$ system



Bulk Defects

- **Pores** (*esp. ceramics*) - can greatly affect optical, thermal, mechanical properties
- **Cracks** - can greatly affect mechanical properties
- **Foreign inclusions** - can greatly affect electrical, mechanical, optical properties

SUMMARY

- **Point, Line, and Area** defects arise 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.)