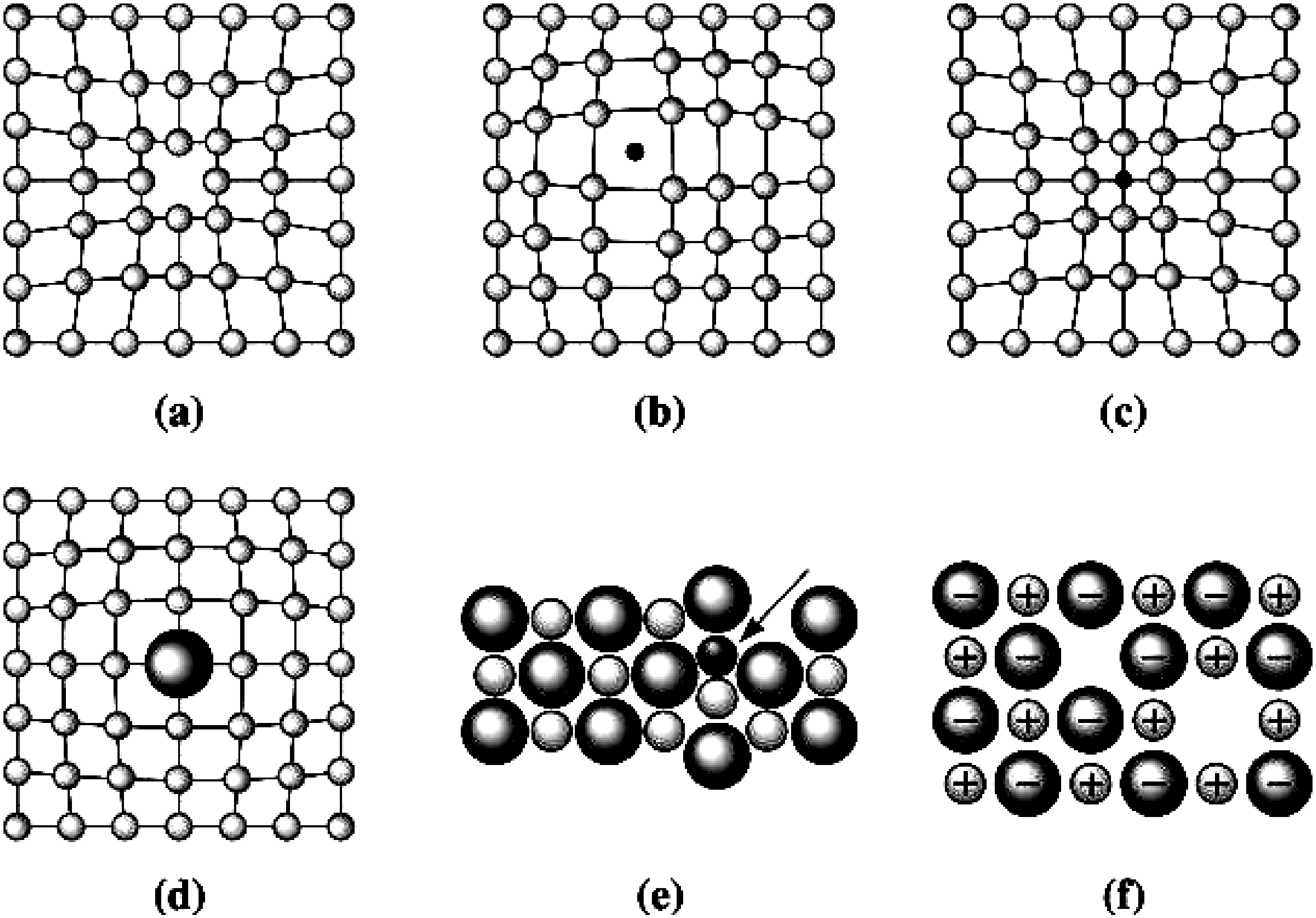
Lecture Outline Real Structure

- ☐ Point Defects (zero-dimensional) – they move by diffusion
- ☐ Line defects – Dislocations, one-dimensional – they move by glide
- ☐ Observing Dislocations
- ☐ Significance of Dislocations
- ☐ Schmid’s Law
- ☐ Influence of Crystal Structure
- ☐ Plane (area) Defects, (two-dimensional)
- ☐ Volume Defects (three-dimensional)

Point Defects

- Point defects – essentially “zero dimensional” imperfections, such as vacancies, that are located typically at one (in some cases a few) sites in the crystal.
- Vacancy - An atom or an ion missing from its regular crystallographic site.
- Interstitial defect - A point defect produced when an atom is placed into the crystal at a site that is normally not a lattice point. Also an “alien” atom in one of the interstitials in a structure
- Substitutional defect - A point defect produced when an atom is removed from a regular lattice point and replaced with a different atom, usually of a different size.
- Extended defects - Defects that involve several atoms/ions and thus occur over a finite volume of the crystalline material (e.g., dislocations, stacking faults, grain boundary).

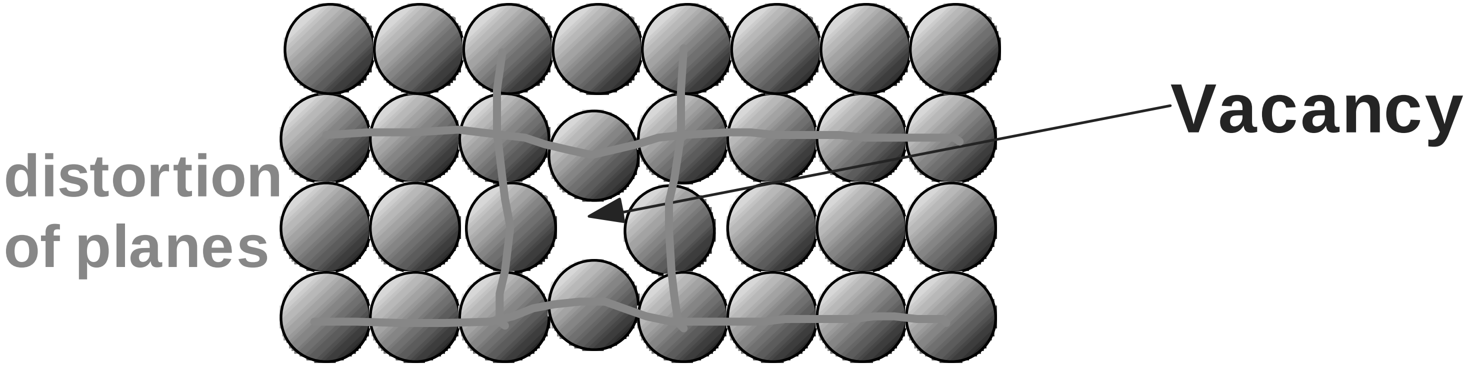
- **Point defects being “OD” entities, dislocations are a line of defects defect, 1D; stacking faults/grain boundaries are a plane of defects, 2D; alien phases or voids are a volume of defects, 3D**


(a) (b) (c)
(d) (e) (f)

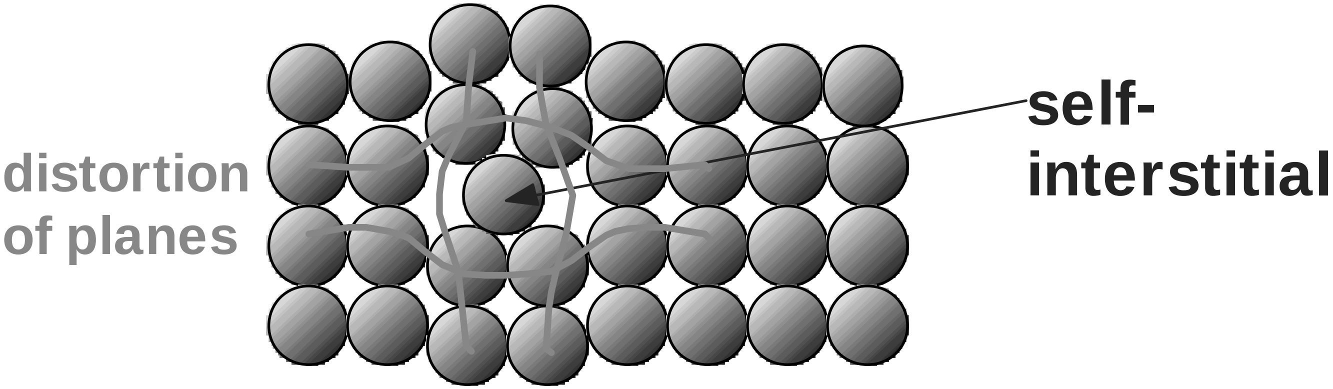
Point defects: (a) vacancy, (b) interstitial atom, (c) small substitutional atom, (d) large substitutional atom, (e) Frenkel defect – ionic crystals (f) Schottky defect – ionic crystals. All of these defects disrupt the perfect arrangement of the surrounding atoms.

Why do we have POINT DEFECTS ?

- **Vacancies:**
  -vacant atomic sites in a structure.



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



Surely, distortion of planes means excess elastic energy, things in nature – when left alone - always go to states of lowest energy, so how come point defects are here to stay?

$$G = E - TS + pV$$

minimization of Gibbs free energy decided which structures are stable,

E is internal energy, if there are point defects this term is higher

S is entropy: a measure for the disorder in a system, it there are point defects, entropy is higher

T is temperature

P is pressure

V is volume

So G is smaller for a certain concentration of point defect at a certain temperature, when the increase in the second term outweighs the increase in the first term

EQUIL. CONCENTRATION: POINT DEFECTS

- **varies with temperature!**

No. of defects

Activation energy

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

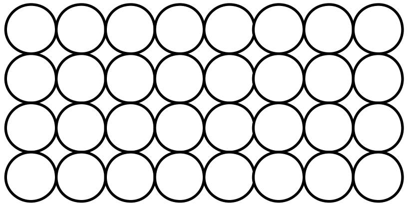
Temperature

No. of potential defect sites.

Boltzmann's constant

$(1.38 \times 10^{-23}$ J/atom K)

$(8.62 \times 10^{-5}$ eV/atom K)



Each lattice site is a potential vacancy site

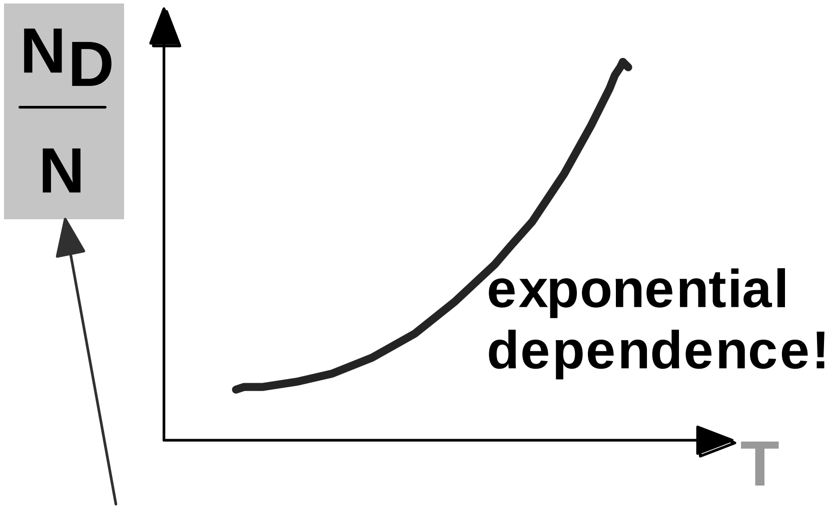
Activation energies may also be quoted in J per mole, or cal/mol, then the product of Boltzmann’s constant and Avogadro’s constant is to be used in order to consider single atoms

MEASURING ACTIVATION ENERGY

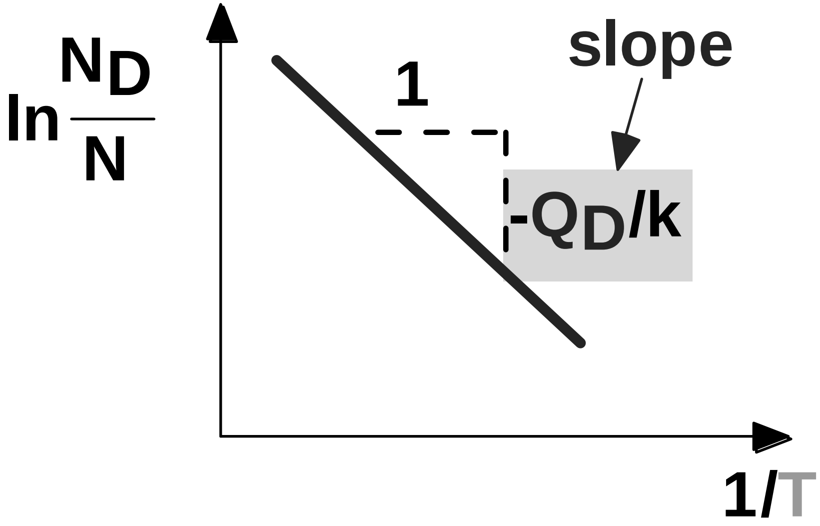
- **We can get Q from an experiment.**

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

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



defect concentration



Arrhenius plot

ESTIMATING VACANCY concentration

Find equilibrium of vacancies in 1m^3 of Cu at 1000 ºC.

- **Given:**

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

$Q_V = 0.9\mathrm{eV/atom}$ $\quad N_A = 6.02 \times 10^{23}$ atoms/mole

0.9eV/atom

$$\frac{N_D}{N} = \exp\left(\frac{-Q_D}{kT}\right) = 2.7 \cdot 10^{-4}$$

1273K

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

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

- **Answer:**

$N_D = 2.7 \cdot 10^{-4} \cdot 8.0 \times 10^{28}$ **sites** $= 2.2 \times 10^{25}$ **vacancies**

The Effect of Temperature on Vacancy Concentrations

Calculate the concentration of vacancies in copper at room temperature (25^{o}C). What temperature will be needed to heat treat copper such that the concentration of vacancies produced will be 1000 times more than the equilibrium concentration of vacancies at room temperature? Assume that 20,000 cal are required to produce a mole of vacancies in copper.

SOLUTION

The lattice parameter of FCC copper is 0.36151 nm. The basis is 1, therefore, the number of copper atoms, or lattice points, per cm^3 is:

$$n = \frac{4\text{ atoms/cell}}{(3.6151 \times 10^{-8}\text{ cm})^3} = 8.47 \times 10^{22}\text{ copper atoms/cm}^3$$

SOLUTION (Continued)

At room temperature, T = 25 + 273 = 298 K:

$$n_n = n \exp\left(\frac{Q_n}{RT}\right)$$

$$= \left(8.47 \times 10^{22} \ \frac{\text{atoms}}{\text{cm}^3}\right). \ \exp\left(\frac{-\ 20{,}000 \ \dfrac{\text{cal}}{\text{mol}}}{1.987 \ \dfrac{\text{cal}}{\text{mol} - \text{K}} \times 298\text{K}}\right)$$

$$= 1.815 \times 10^{8} \text{ vacancies/cm}^{3}$$

We could do this by heating the copper to a temperature at which this number of vacancies forms:

$$n_n = 1.815 \times 10^{11} = n \exp\left(\frac{Q_n}{RT}\right)$$

$$= (8.47 \times 10^{22}) \exp(-20{,}000 \,/(1.987 \times T)), \ \ T = 102^{\text{o}}\text{C}$$

Vacancy Concentrations in Iron

Determine the number of vacancies needed for a BCC iron crystal to have a density of 7.87 g/cm^3. The lattice parameter of the iron is 2.866×10^{-8} cm.

SOLUTION

The expected theoretical density of iron can be calculated from the lattice parameter and the atomic mass.

$$\rho = \frac{(2 \text{ atoms/cell})(55.847 \text{ g/mol})}{(2.866 \times 10^{-8} \text{ cm})^3 (6.02 \times 10^{23} \text{ atoms/mol})} = 7.8814 \text{ g/cm}^3$$

SOLUTION (Continued)

Let's calculate the number of iron atoms and vacancies that would be present in each unit cell for the required density of 7.87 g/cm^3:

$$\rho = \frac{(X \text{ atoms/cell})(55.847 \text{ g/mol})}{(2.866 \times 10^{-8} \text{ cm})^3 (6.02 \times 10^{23} \text{ atoms/mol})} = 7.87 \text{ g/cm}^3$$

$$X \text{ atoms/cell} = \frac{(7.87)(2.866 \times 10^{-8})^3 (6.02 \times 10^{23})}{55.847} = 1.9971$$

Or, there should be 2.00 – 1.9971 = 0.0029 vacancies per unit cell. The number of vacancies per cm^3 is:

$$\text{Vacancies/cm}^3 = \frac{0.0029 \text{ vacancies/cell}}{(2.866 \times 10^{-8} \text{ cm})^3} = 1.23 \times 10^{20}$$

Sites for Carbon in Iron

In FCC iron, carbon atoms are located at *octahedral* sites at the center of each edge of the unit cell (1/2, 0, 0) and at the center of the unit cell (1/2, 1/2, 1/2). In BCC iron, carbon atoms enter tetrahedral sites, such as 1/4, 1/2, 0. The lattice parameter is 0.3571 nm for FCC iron and 0.2866 nm for BCC iron. Assume that carbon atoms have a radius of 0.071 nm. (1) Would we expect a greater distortion of the crystal by an interstitial carbon atom in FCC or BCC iron? (2) What would be the atomic percentage of carbon in each type of iron if all the interstitial sites were filled?

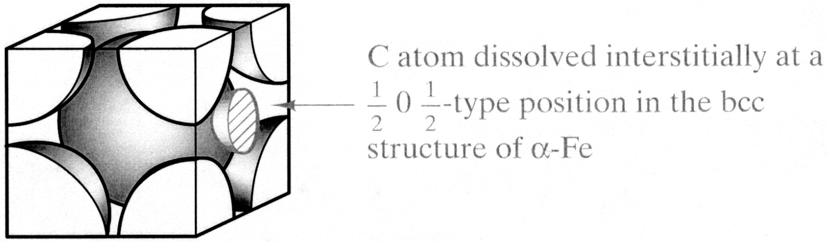
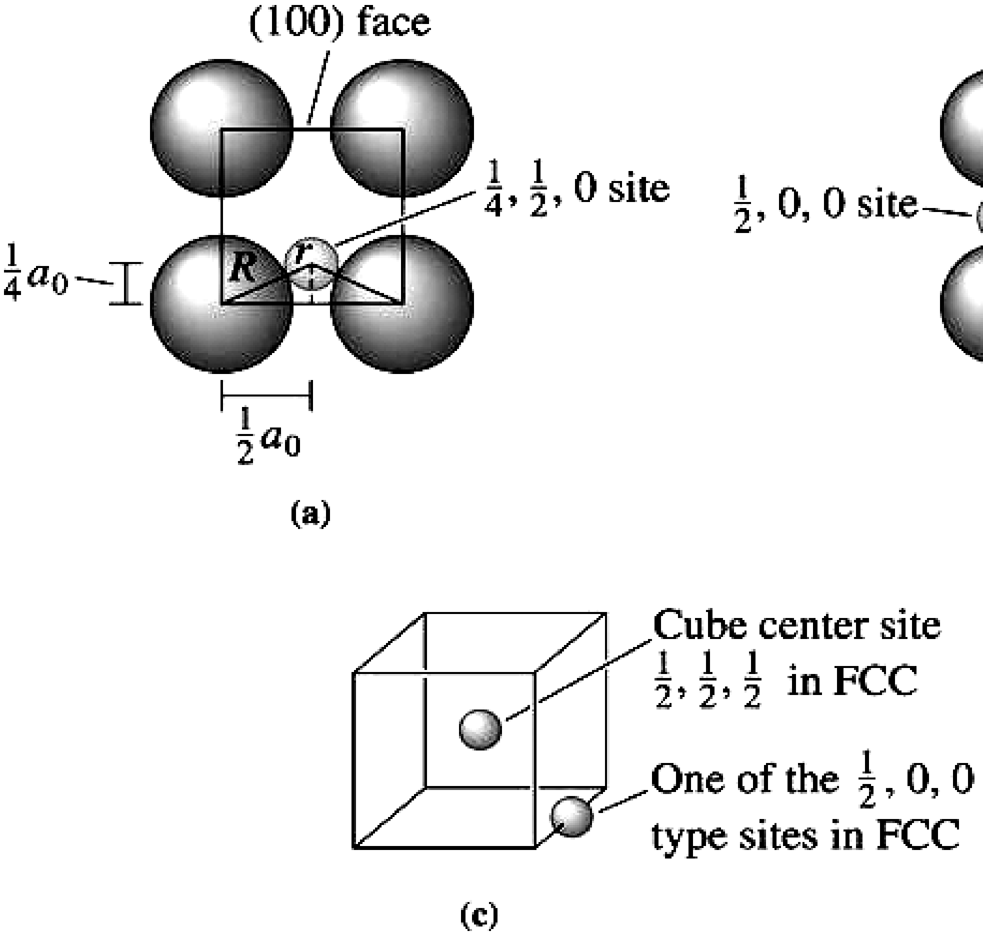


Figure 4-4 *Interstitial solid solution of carbon in α-iron. The carbon atom is small enough to fit with some strain in the interstice (or opening) among adjacent Fe atoms in this structure of importance to the steel industry. [This unit cell structure can be compared with Figure 3–4b.]*



(a) The location of the ¼, ½, 0 interstitial site in BCC metals, showing the arrangement of the normal atoms and the interstitial atom (b) ½, 0, 0 site in FCC metals, (c) Edge centers and cube centers are some of the interstitial sites in the FCC structure.

SOLUTION

1. We could calculate the size of the interstitial site at the 1/4, 1/2, 0 location with the help of Figure 4.2(a). The radius R_{BCC} of the iron atom is:

$$R_{\text{BCC}} = \frac{\sqrt{3}a_0}{4} = \frac{(\sqrt{3})(0.2866)}{4} = 0.1241 \text{ nm}$$

From Figure 4.2(a), we find that:

$$\left(\frac{1}{2}a_0\right)^2 + \left(\frac{1}{4}a_0\right)^2 = (r_{\text{interstitial}} + R_{\text{BCC}})^2$$

$$r_{\text{interstitial}} = \sqrt{0.02567} - 0.1241 = 0.0361 \text{ nm}$$

For FCC iron, the interstitial site such as the 1/2, 0, 0 lies along $\langle 100 \rangle$ directions. Thus, the radius of the iron atom and the radius of the interstitial site are

SOLUTION (Continued)

$$R_{\text{FCC}} = \frac{\sqrt{2}a_0}{4} = \frac{(\sqrt{2})(0.3571)}{4} = 0.1263 \text{ nm}$$

$$2r_{\text{interstitial}} + 2R_{\text{FCC}} = a_0$$

$$r_{\text{interstitial}} = \frac{0.3571 - (2)(0.1263)}{2} = 0.0522 \text{ nm}$$

The interstitial site in the BCC iron is smaller than the interstitial site in the FCC iron. Although both are smaller than the carbon atom, carbon distorts the BCC crystal structure more than the FCC crystal. As a result, fewer carbon atoms are expected to enter interstitial positions in BCC iron than in FCC iron.

SOLUTION (Continued)

2. We can find a total of 24 interstitial sites of the type 1/4, 1/2, 0; however, since each site is located at a face of the unit cell, only half of each site belongs uniquely to a single cell. Thus:
   (24 sites)(1/2) = 12 interstitial sites per unit cell

   Atomic percentage of carbon in BCC iron would be:

$$\text{at \% C} = \frac{12\ \text{C atoms}}{12\ \text{C atoms} + 2\ \text{Fe atoms}} \times 100 = 86\%$$

In FCC iron, the number of octahedral interstitial sites is:
(12 edges) (1/4) + 1 center = 4 interstitial sites per unit cell

Atomic percentage of carbon in BCC iron would be:

$$\text{at \% C} = \frac{4\ \text{C atoms}}{4\ \text{C atoms} + 4\ \text{Fe atoms}} \times 100 = 50\%$$

Dopants in Germanium Semiconductor

Three separate samples of germanium (Ge) crystals contain small concentrations of either silicon (Si), arsenic (As), or boron (B) as dopants. Based on the valence of these elements, what type of semiconductivity is expected from these materials? Assume that these elements will occupy Ge sites.

SOLUTION

When Si is added to Ge, silicon atoms can form four bonds with neighboring Ge atoms. As a result, there is no need to donate or accept an electron. The resultant material then does not show either ‘‘*n*-type’’ or ‘‘*p*-type’’ conductivity.

When we add As, we expect *n*-type conductivity since each As atom brings in five valence electrons.

When we add small concentrations of B to Ge we expect *p*-type conductivity for the resultant material, since B has a valence of 3.

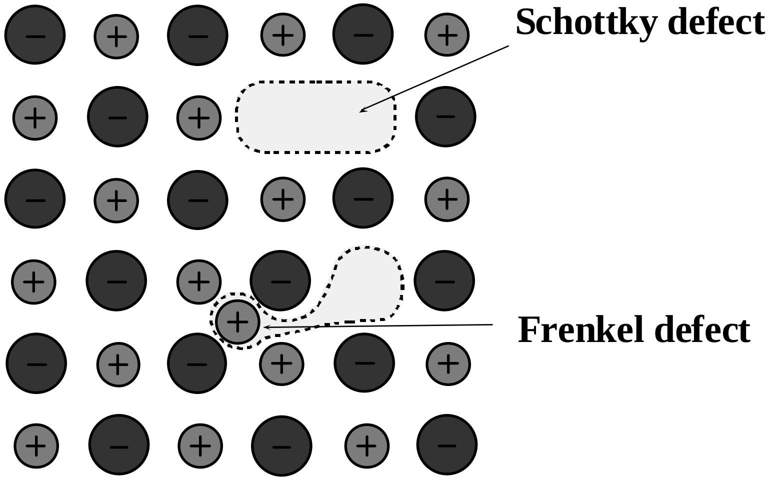
Other Point Defects

☐ Interstitialcy - A point defect caused when a ‘‘normal’’ atom occupies an interstitial site in the crystal.

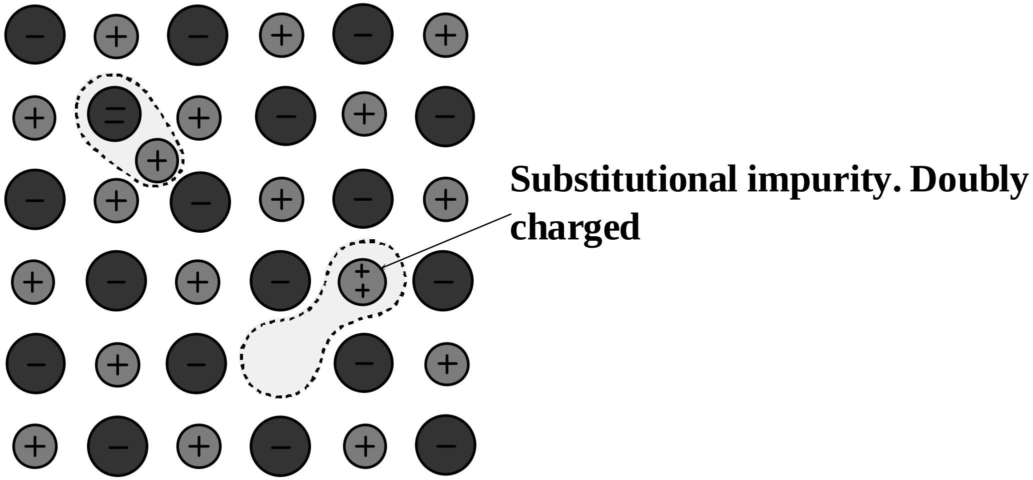
in ionic crystals

☐ Frenkel defect - A pair of point defects produced when an ion moves to create an interstitial site, leaving behind a vacancy.

☐ Schottky defect - A point defect in ionically bonded materials. In order to maintain a neutral charge, a stoichiometric number of cation and anion vacancies must form.

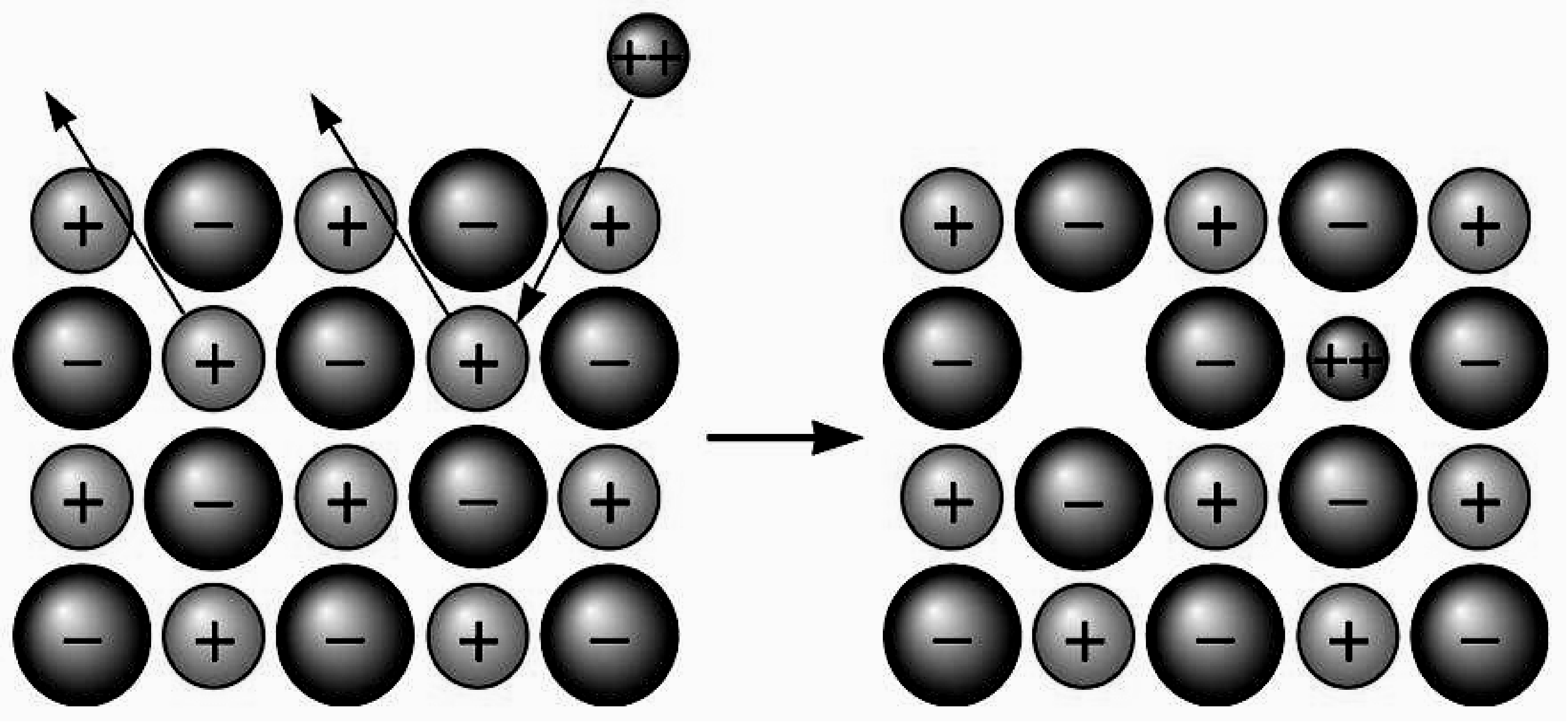


(a) Schottky and Frenkel defects in an ionic crystal.



(b) Two possible imperfections caused by ionized substitutional impurity atoms in an ionic crystal.

Fig. 1.45: Point defects in ionic crystals

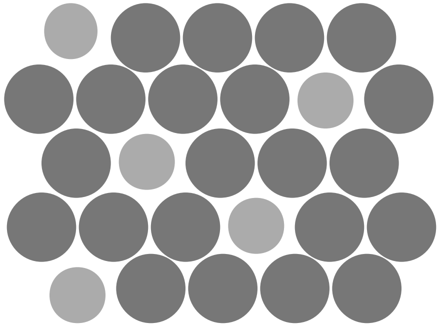


As for divalent anions, so for divalent cations, when a divalent cation replaces a monovalent cation, a second monovalent cation must also be removed, creating a vacancy.

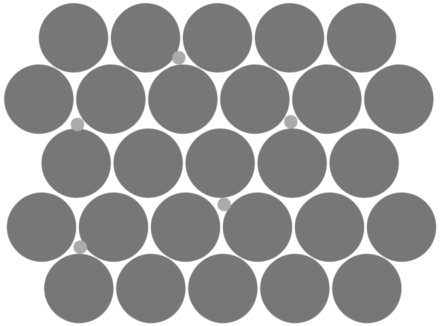
point defects in alloys

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

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



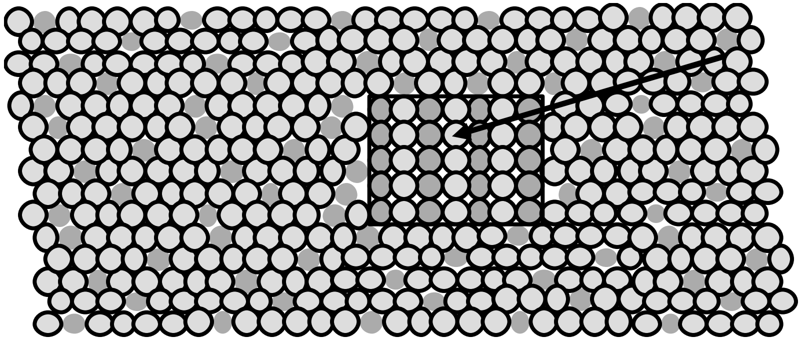
OR



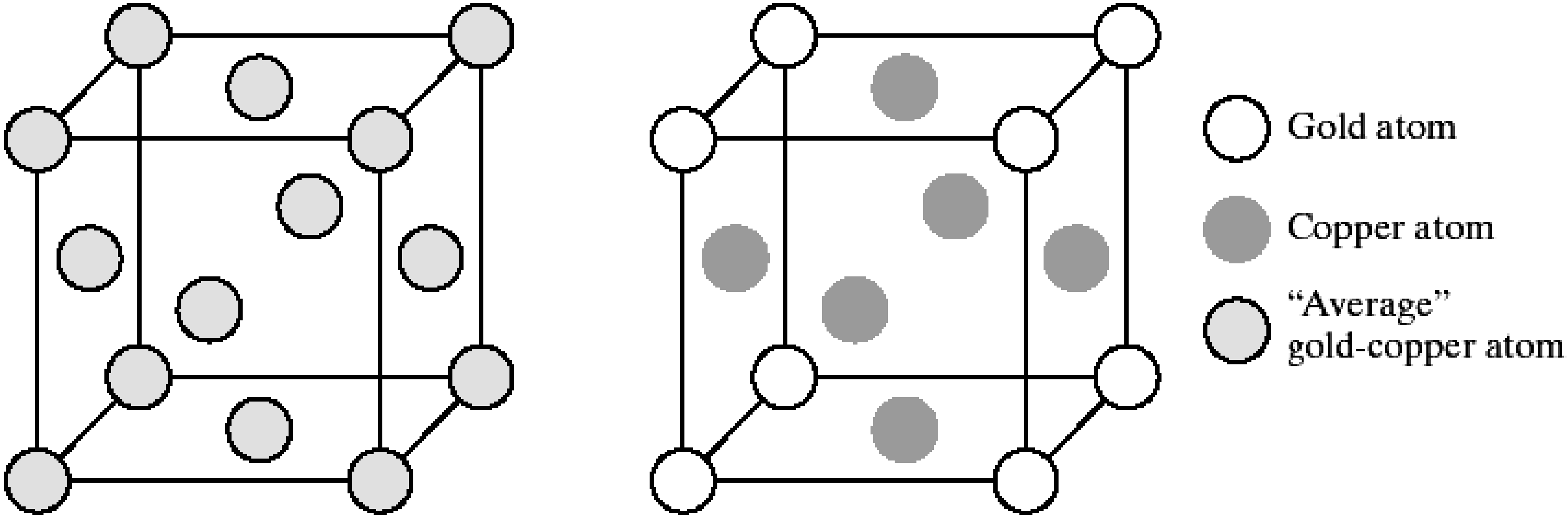
Substitutional alloy (e.g., Cu in Ni)

Interstitial alloy (e.g., C in Fe)

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

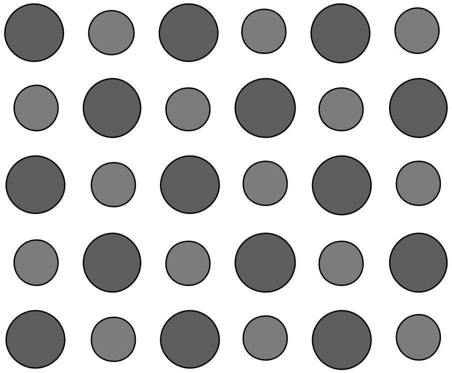


Second phase particle
--different composition
--often different crystal structure,
so that is really a volume defect.



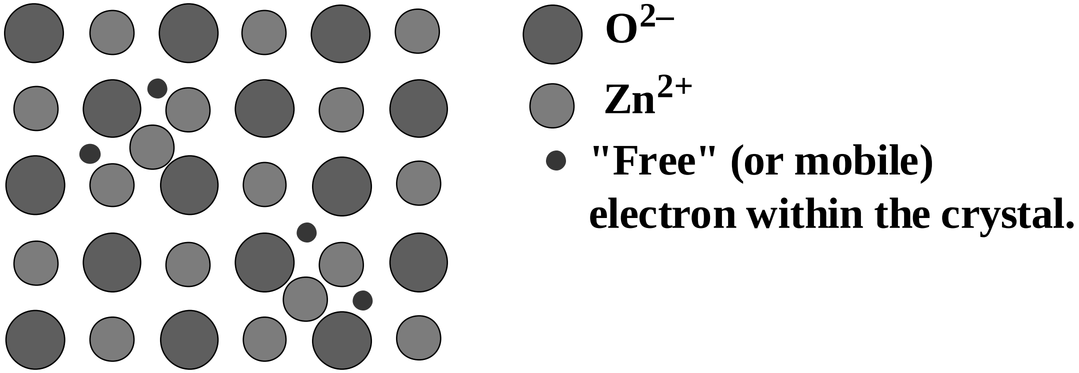
(a) Disordered (b) Ordered

Figure 4-3 *Ordering of the solid solution in the* $AuCu_3$ *alloy system. (a) Above* ~ 390°*C, there is a random distribution of the Au and Cu atoms among the fcc sites. (b) Below* ~ 390°*C, the Au atoms preferentially occupy the corner positions in the unit cell, giving a simple cubic Bravais lattice. (From B. D. Cullity,* Elements of X-Ray Diffraction, *2nd ed., Addison-Wesley Publishing Co., Inc., Reading, Mass., 1978.)*



(a) Stoichiometric ZnO crystal with equal number of anions and cations and no free electrons.

Large changes in electric conductivity /resistivity are observed for slight changes in stoichiometry



(b) Non-Stoichiometric ZnO crystal with excess Zn in interstitial sites as Zn^{2+} cations.

Fig. 1.54: Stoichiometry and nonstoichiometry and the resulting defect structure.

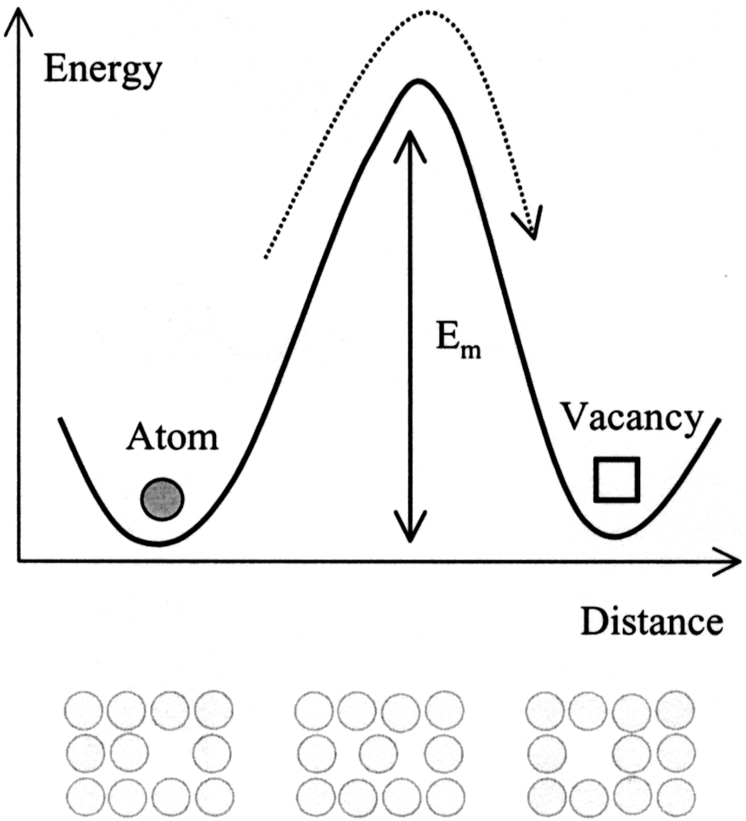
(a) Perfect crystal without vacancies

(b) An energetic atom at the surface breaks bonds and jumps on to a new adjoining position on the surface. This leaves behind a vacancy.

(c) An atom in the bulk diffuses to fill the vacancy thereby displacing the vacancy towards the bulk.

(d) Atomic diffusions cause the vacancy to diffuse into the bulk.

Fig. 1.43: Generation of a vacancy by the diffusion of an atom to the surface and the subsequent diffusion of the vacancy into the bulk.



Schematic representation of the diffusion of an atom from its original position into a vacant lattice site. At activation energy E_m has to be supplied to the atom so that it could break inter-atomic bonds and to move into the new position.

How are point defects generated and moving?

Diffusion, a thermally activated process, it thermal takes energy to over the diffusion barrier

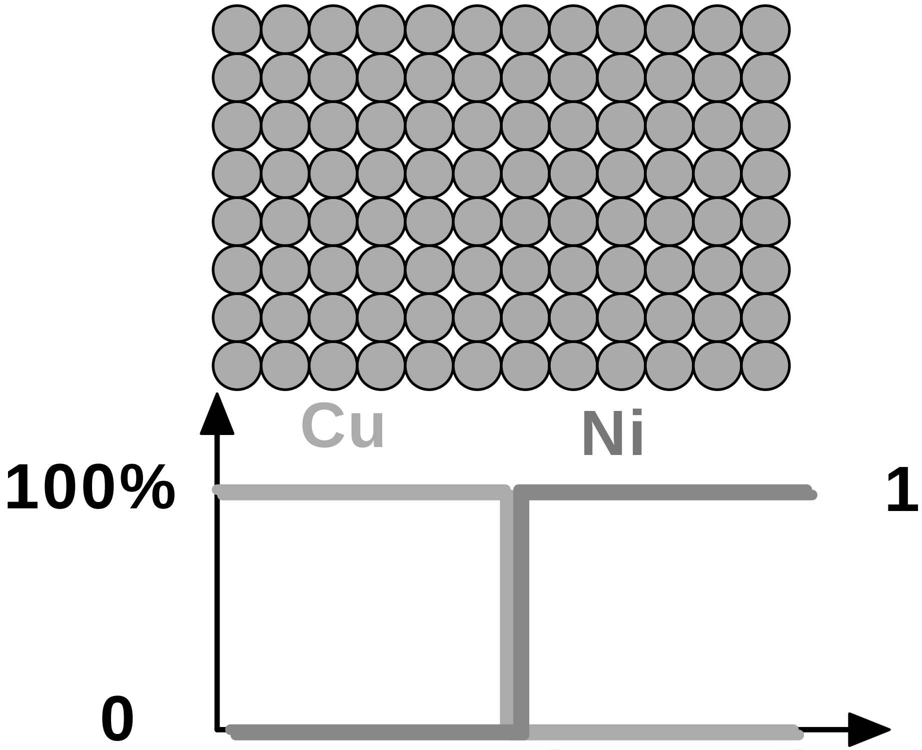
happens at all temperatures, gets really fast at high temperature, in melts and vapour,

is very important for changes in the microstructure of crystals

diffusion: the phenomena I

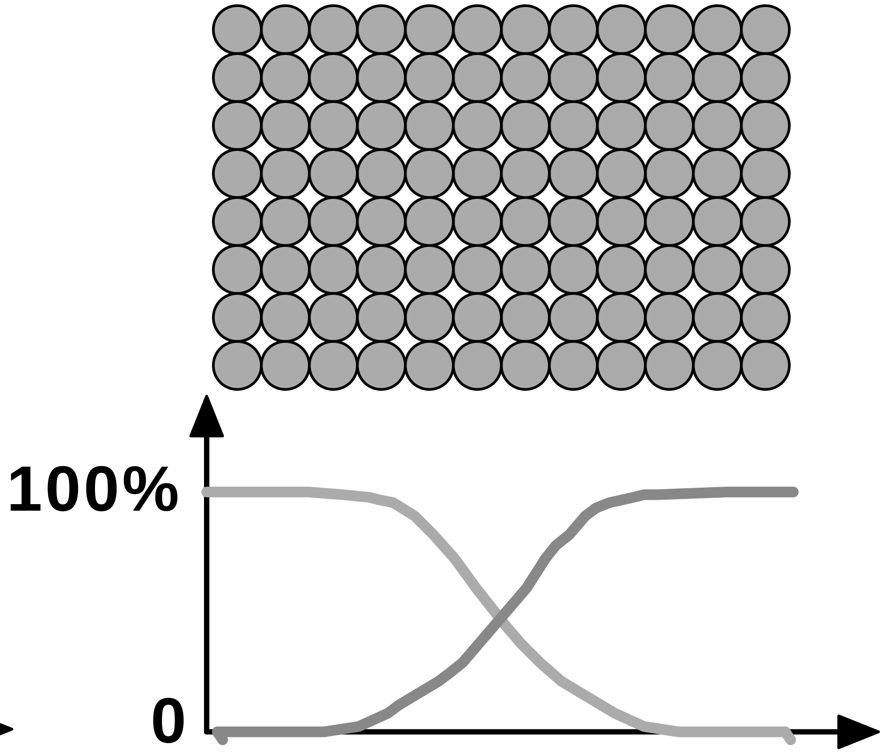
- **Interdiffusion:** **In an alloy, atoms tend to migrate from regions of large concentration.**

Initially



Concentration Profiles

After some time

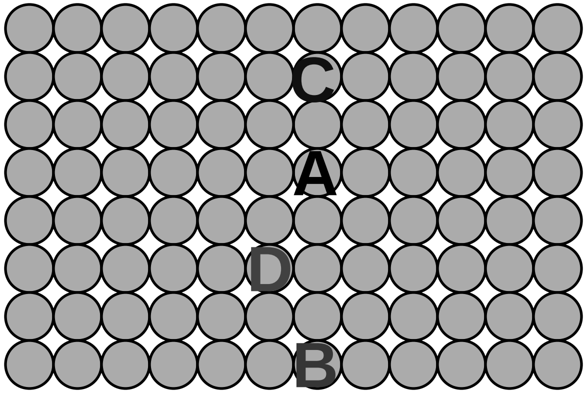


Concentration Profiles

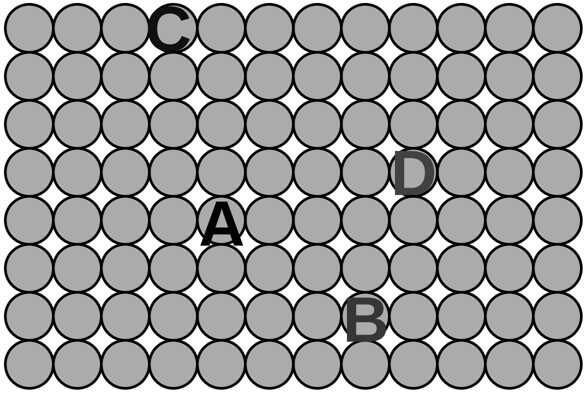
diffusion: the phenomena (II)

- **Self-diffusion:** **In an elemental solid, atoms also migrate.**

Label some atoms

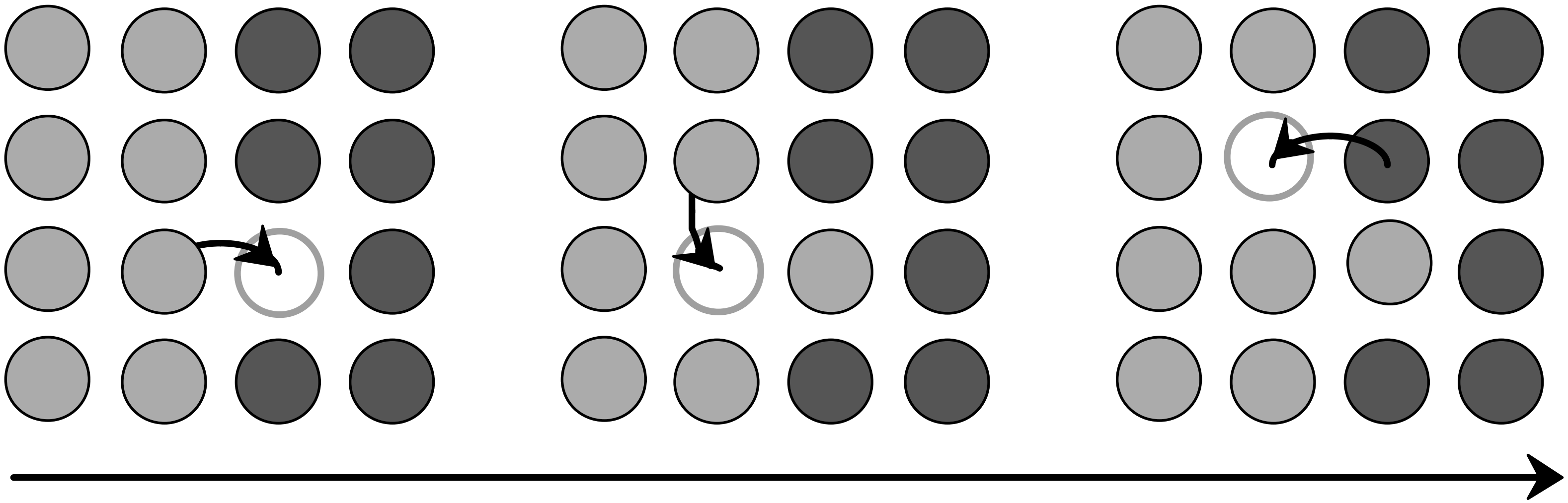


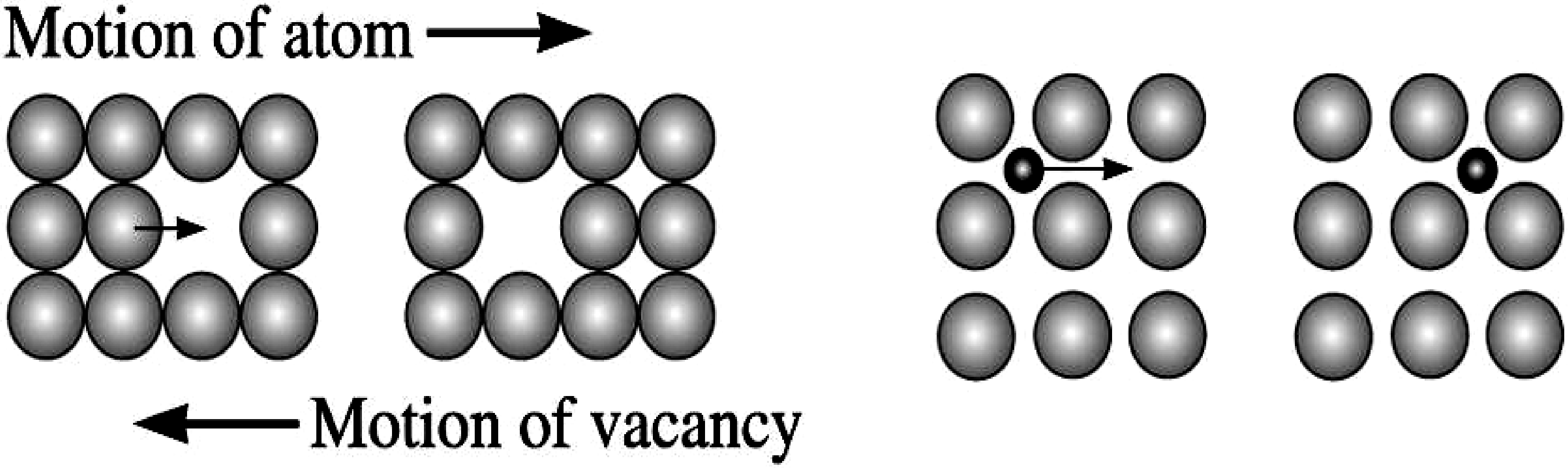
After some time



Substitutional Diffusion:

- applies to substitutional impurities
- atoms exchange with vacancies
- rate depends on:
  --number of vacancies
  --activation energy to exchange.


increasing elapsed time



(a) Vacancy mechanism

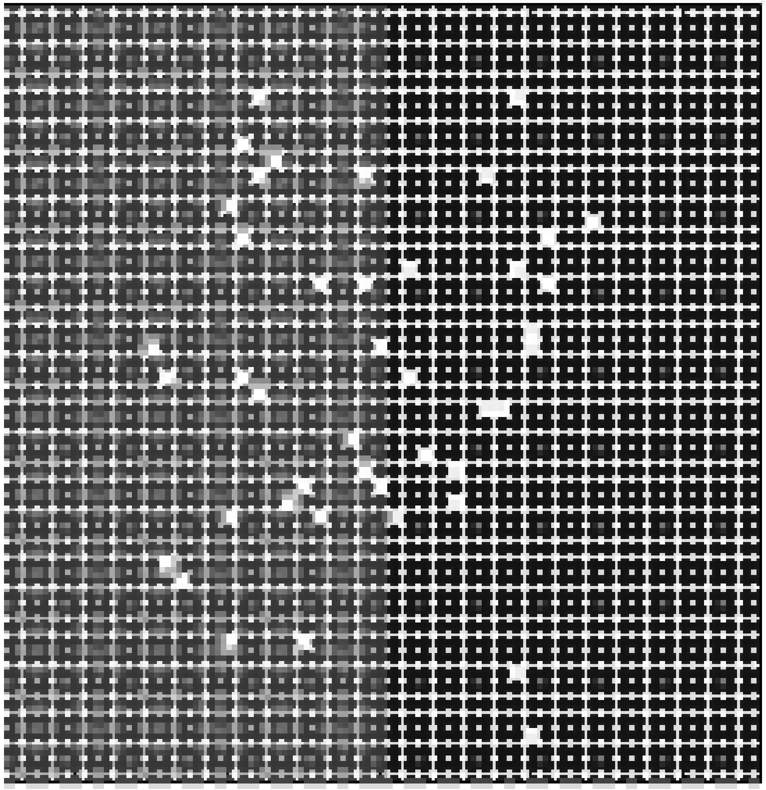
(b) Interstitial mechanism

Diffusion mechanisms in material: (a) vacancy or substitutional atom diffusion and (b) interstitial diffusion. The vacancies move in the opposite direction to the atoms

diffusion simulation

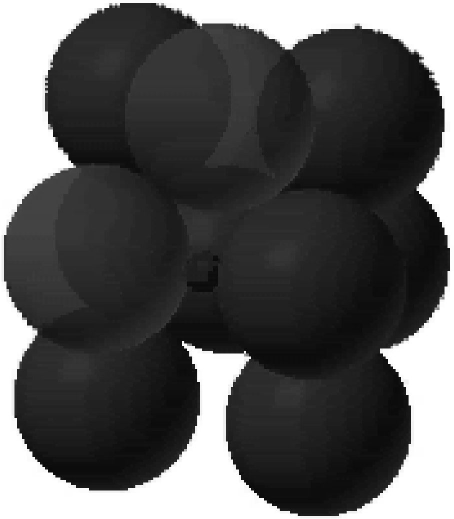
- **Simulation of interdiffusion across an interface:**

- **Rate of substitutional diffusion depends on:**
  - **--vacancy concentration**
  - **--frequency of jumping.**

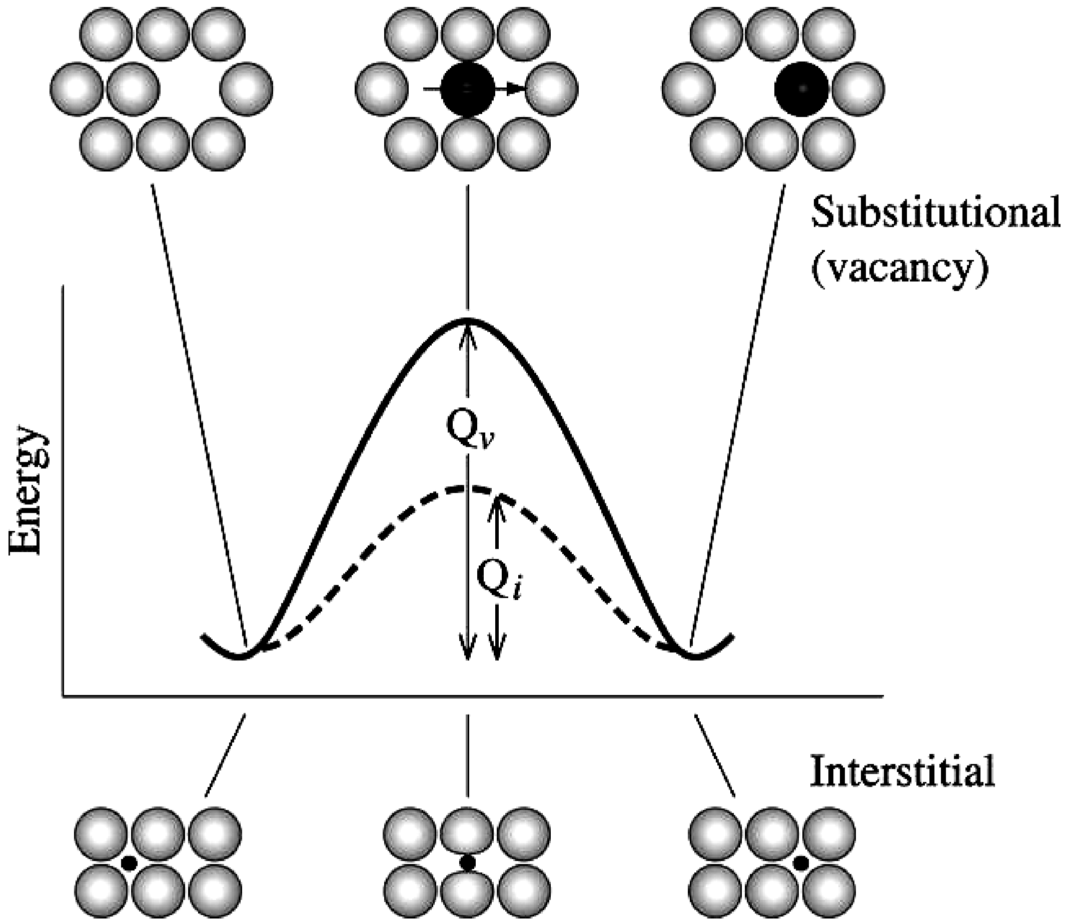


interstitial simulation

- Applies to interstitial impurities.
- More rapid than vacancy diffusion.
- Simulation:
  - -- shows the jumping of a smaller atom (gray) from one interstitial site to another in a BCC structure. The interstitial sites considered here are at midpoints along the unit cell edges.



Why is interstitial diffusion faster



A high energy is required to squeeze atoms past one another during diffusion. This energy is the activation energy *Q*. Generally more energy is required for a substitutional atom than for an interstitial atom

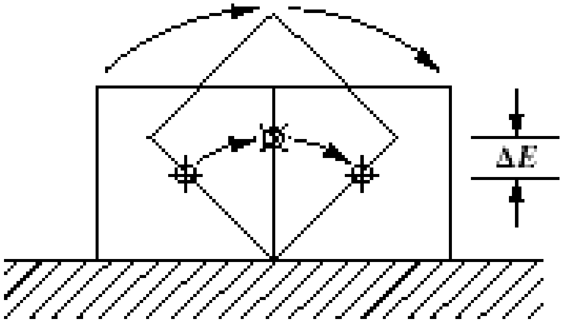
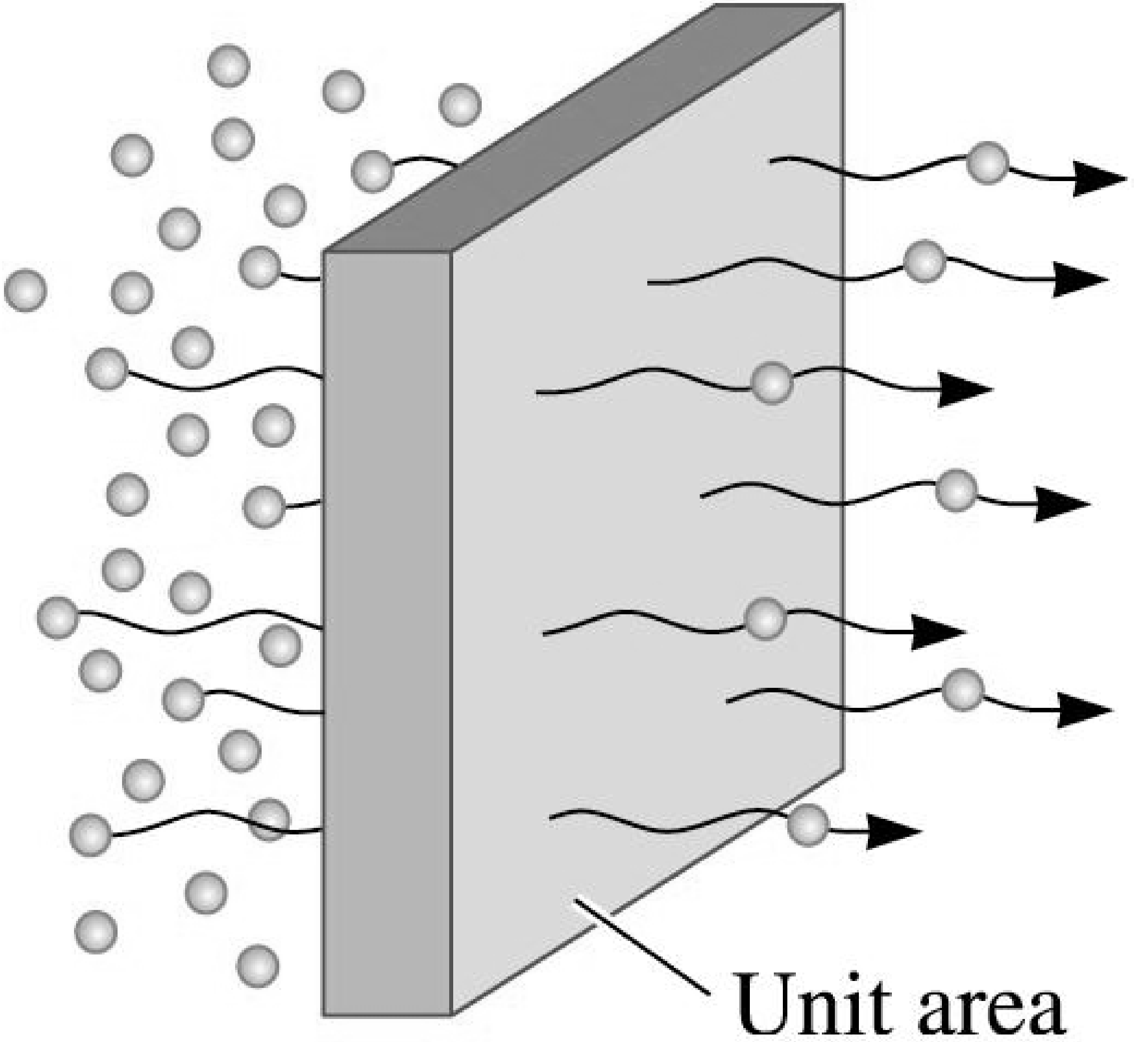


Figure 5-3 *Simple mechanical analog of the process path of Figure 5–2. The box must overcome an increase in potential energy, ΔE, in order to move from one stable position to another.*

Rate of Diffusion (Fick's First Law)

- Fick's first law - The equation relating the flux of atoms by diffusion to the diffusion coefficient and the concentration gradient.
- Diffusion coefficient (D) - A temperature-dependent coefficient related to the rate at which atoms, ions, or other species diffuse.
- Concentration gradient - The rate of change of composition with distance in a nonuniform material, typically expressed as atoms/cm^3·cm or at%/cm.



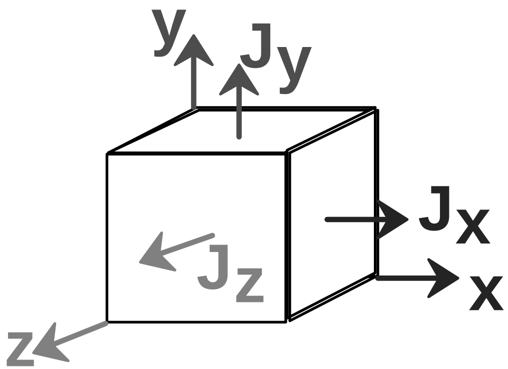
The flux during diffusion is defined as the number of atoms passing through a plane of unit area per unit time

modeling flux

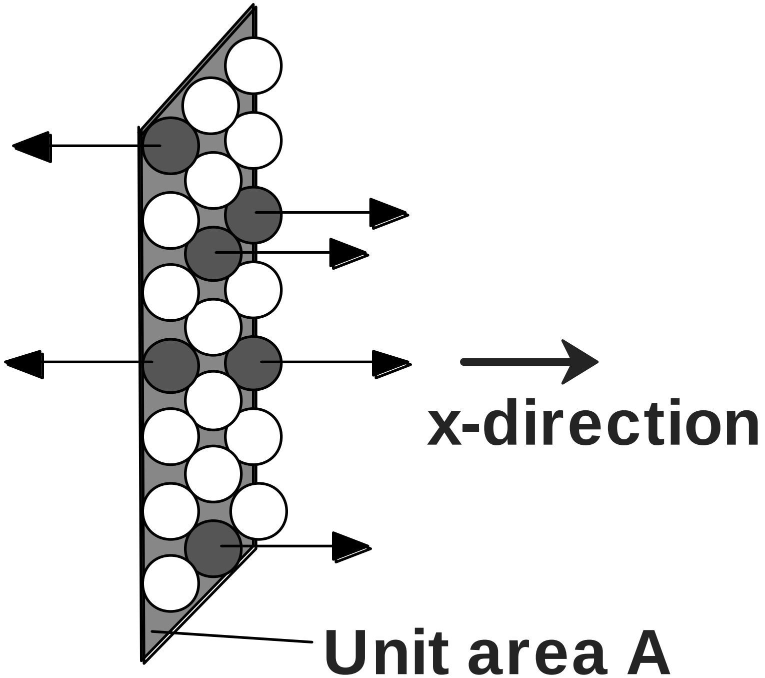
- **Flux:**

$$J = \frac{1}{A}\frac{dM}{dt} \Rightarrow \left[\frac{kg}{m^2 s}\right] \text{ or } \left[\frac{atoms}{m^2 s}\right]$$

- **Directional Quantity**



- **Flux can be measured for:**
  - --vacancies
  - --host (A) atoms
  - --impurity (B) atoms



Unit area A through which atoms move.

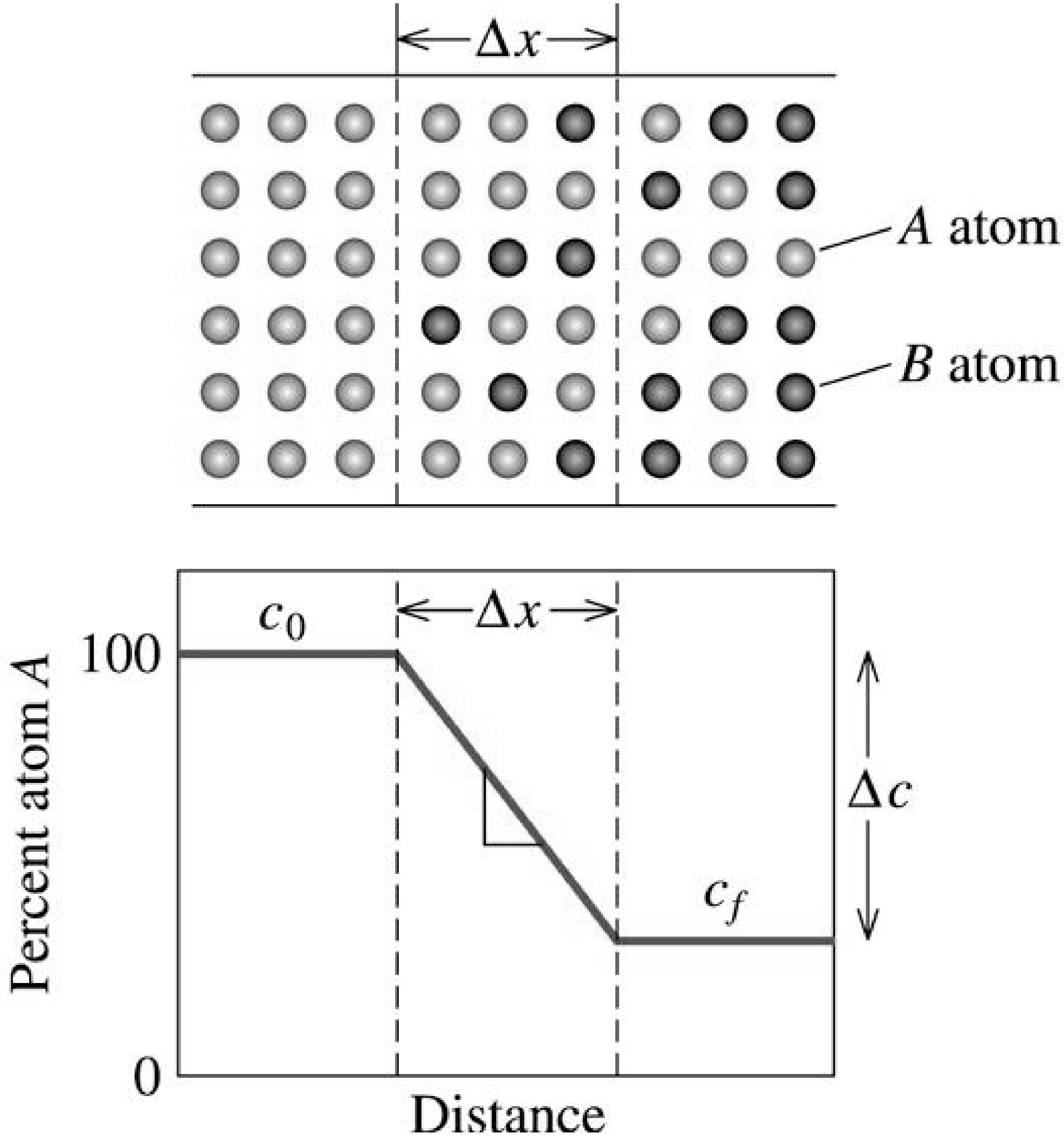


Illustration of the concentration gradient,

mathematically

$$\frac{dc}{dx}$$

concentration gradient & flux

- **Fick's First Law:**

flux in x-dir. [kg/m^2-s]

Diffusion coefficient [m^2/s]

$$J_x = -D \frac{dC}{dx}$$

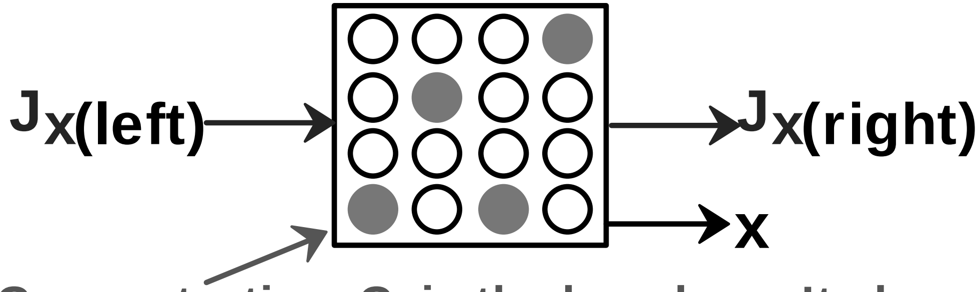
concentration gradient [kg/m^4]

- **The steeper the concentration profile, i.e. the larger the change in this profile = concentration gradient, the the greater the flux!**

The negative sign tells us that the flux is from the higher to the lower concentration

steady state diffusion – no observable result

- **Steady State: the concentration profile doesn't change with time.**



Steady State:

$$J_{x(left)} = J_{x(right)}$$

Concentration, C, in the box doesn't change w/time.

- **Apply Fick's First Law:** $J_x = -D\dfrac{dC}{dx}$

- **If $J_{x(left)} = J_{x(right)}$, then** $\left(\dfrac{dC}{dx}\right)_{left} = \left(\dfrac{dC}{dx}\right)_{right}$

- **Result: the slope, $^{dc}/_{dx}$, must be constant (i.e., slope doesn't vary with position)!**

diffusion and temperature – Arrhenius plots

pre-exponential [m²/s]

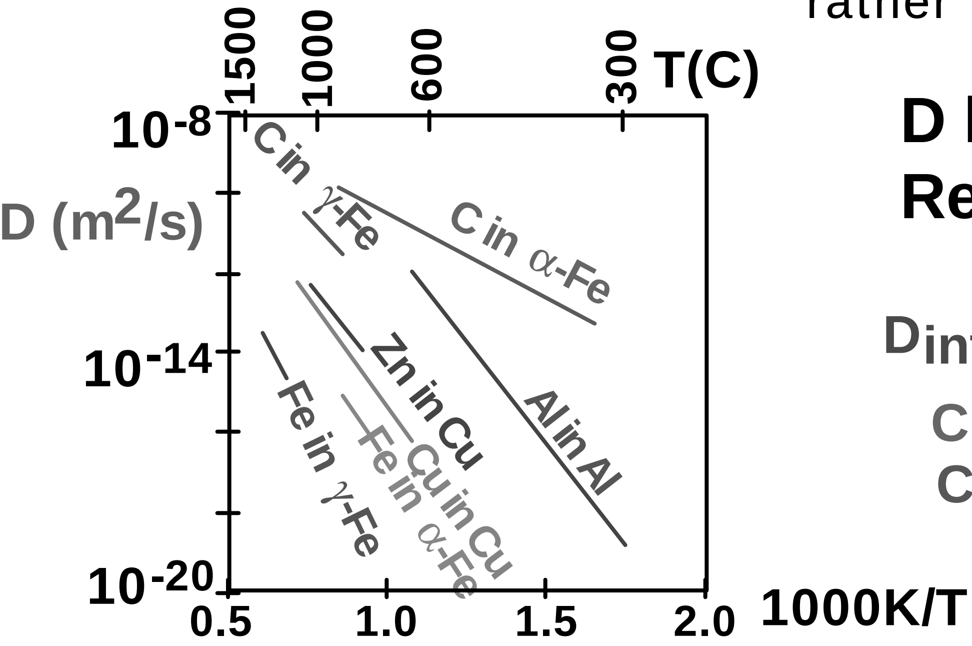
activation energy [J/mol],[eV/mol]

diffusivity $$D = D_o \exp\left(-\frac{Q_d}{RT}\right)$$

gas constant [8.31J/mol-K]

One may as well use Boltzmann’s constant 8.614 10^{-5} eV for considering Q per atom rather than per mol

- **Experimental Data:**

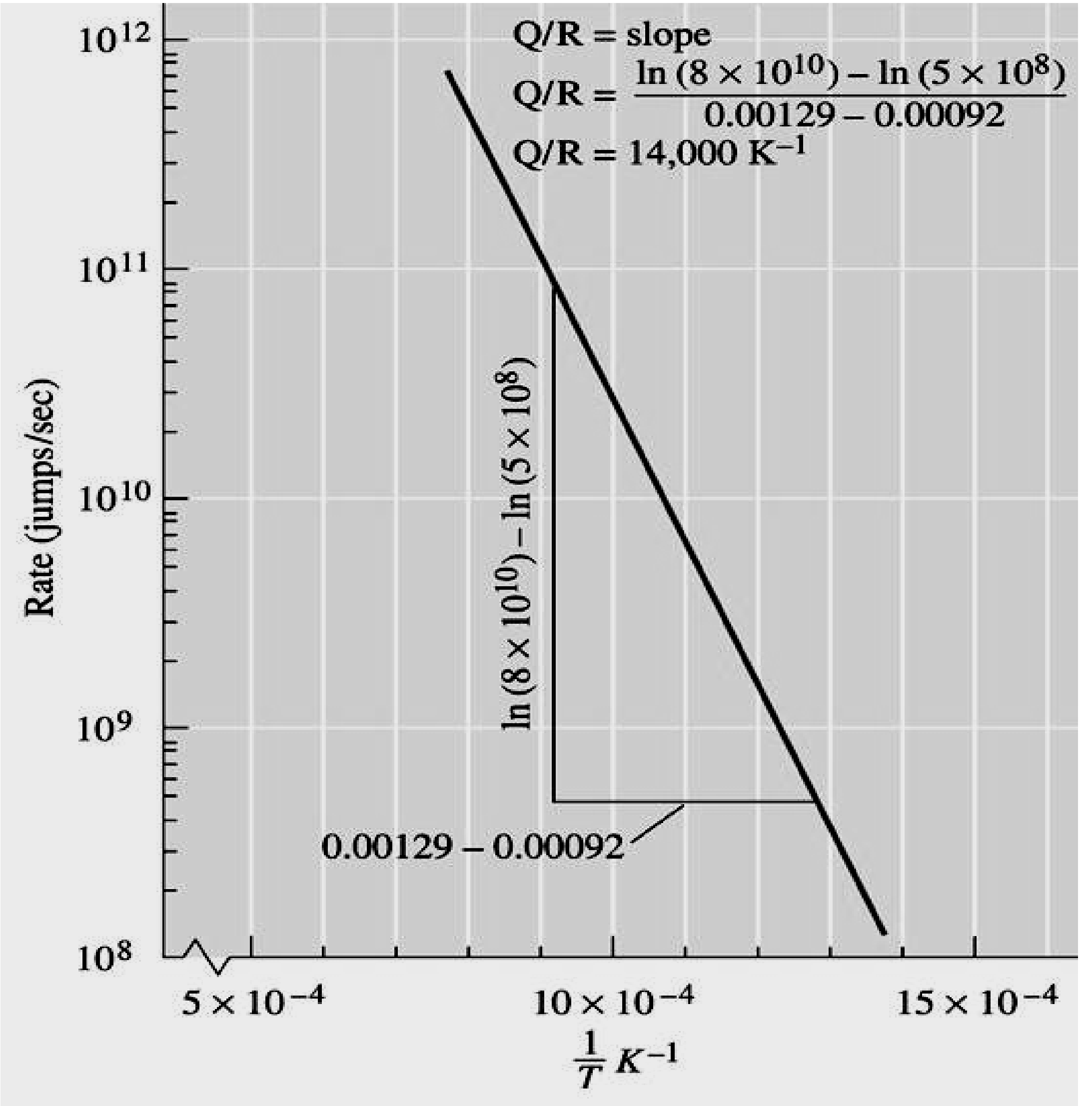


D has exp. dependence on T
Recall: Vacancy does also!

$D_{interstitial} >> D_{substitutional}$

C in α-Fe
C in γ-Fe

Cu in Cu
Al in Al
Fe in α-Fe
Fe in γ-Fe
Zn in Cu



$$D = D_0 \exp\left(\frac{-Q}{RT}\right)$$

Arrhenius plot of in (rate) versus $^1/_T$ can be used to determine the activation energy required for a reaction

Diffusivity (diffusion coefficient) increases exponentially with T.

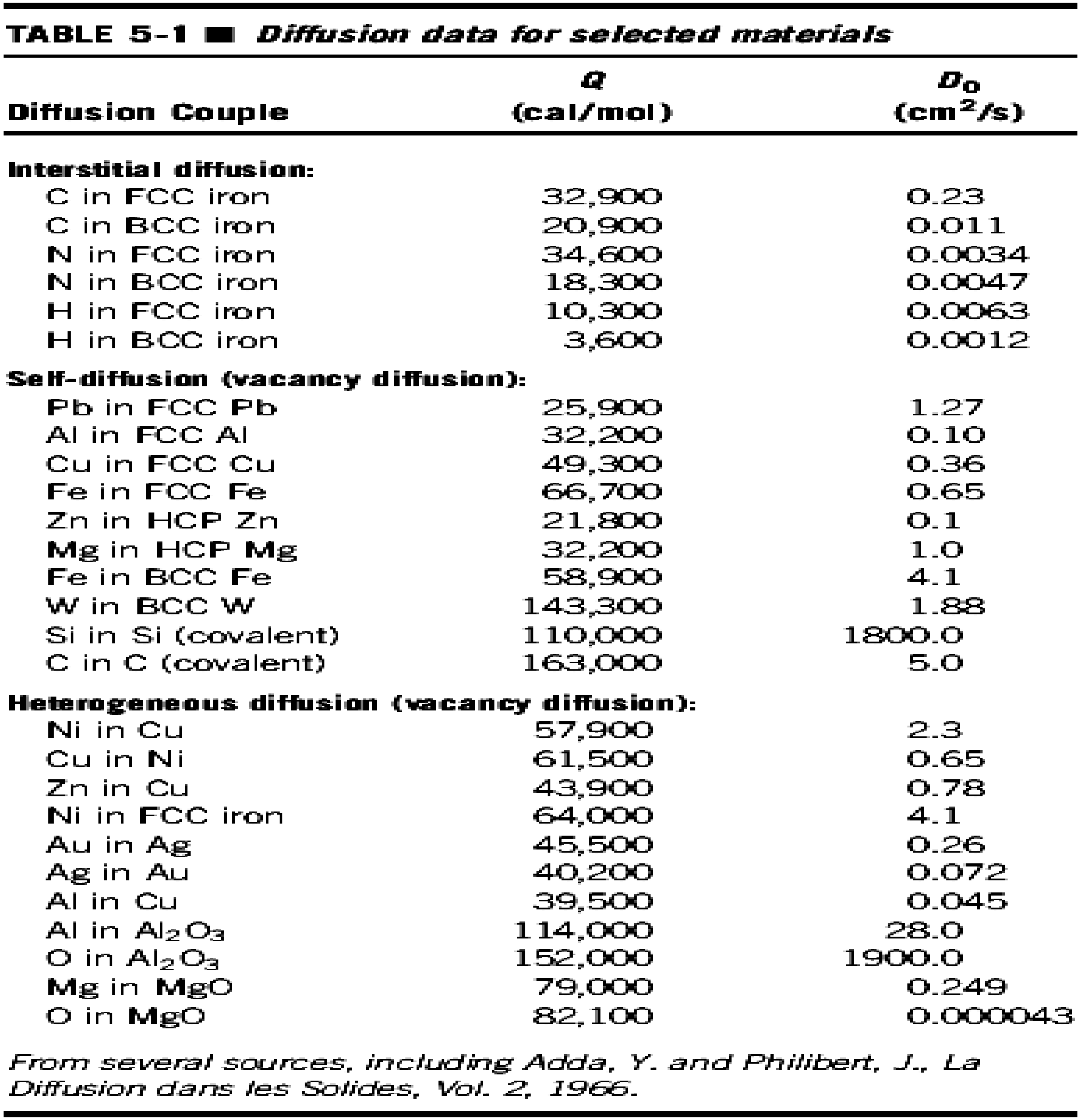


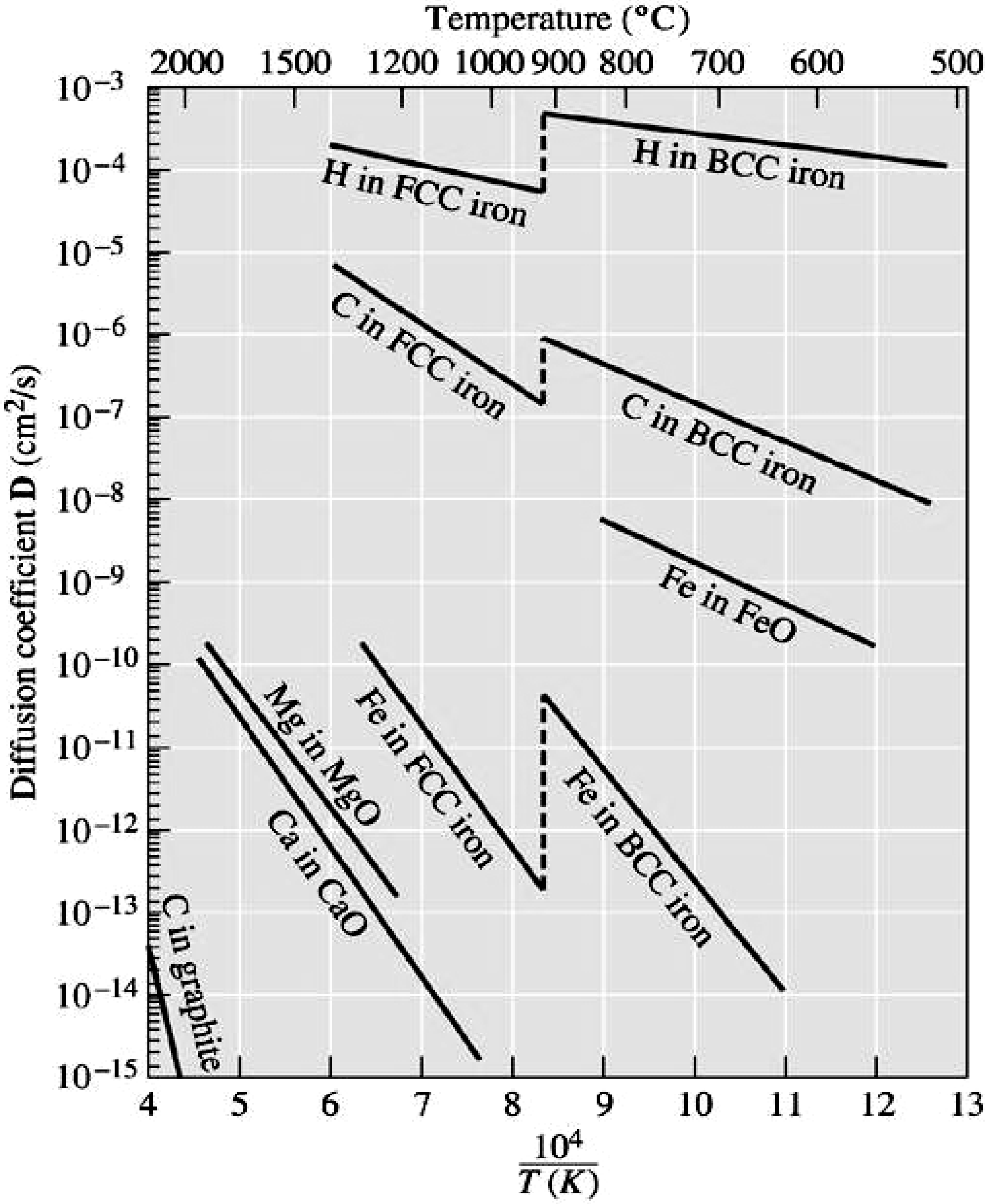
TABLE 5-1 ■ ***Diffusion data for selected materials***

Diffusion Couple	***Q*** **(cal/mol)**	D_0 **(cm²/s)**
Interstitial diffusion:		
C in FCC iron	32,900	0.23
C in BCC iron	20,900	0.011
N in FCC iron	34,600	0.0034
N in BCC iron	18,300	0.0047
H in FCC iron	10,300	0.0063
H in BCC iron	3,600	0.0012
Self-diffusion (vacancy diffusion):		
Pb in FCC Pb	25,900	1.27
Al in FCC Al	32,200	0.10
Cu in FCC Cu	49,300	0.36
Fe in FCC Fe	66,700	0.65
Zn in HCP Zn	21,800	0.1
Mg in HCP Mg	32,200	1.0
Fe in BCC Fe	58,900	4.1
W in BCC W	143,300	1.88
Si in Si (covalent)	110,000	1800.0
C in C (covalent)	163,000	5.0
Heterogeneous diffusion (vacancy diffusion):		
Ni in Cu	57,900	2.3
Cu in Ni	61,500	0.65
Zn in Cu	43,900	0.78
Ni in FCC iron	64,000	4.1
Au in Ag	45,500	0.26
Ag in Au	40,200	0.072
Al in Cu	39,500	0.045
Al in Al_2O_3	114,000	28.0
O in Al_2O_3	152,000	1900.0
Mg in MgO	79,000	0.249
O in MgO	82,100	0.000043

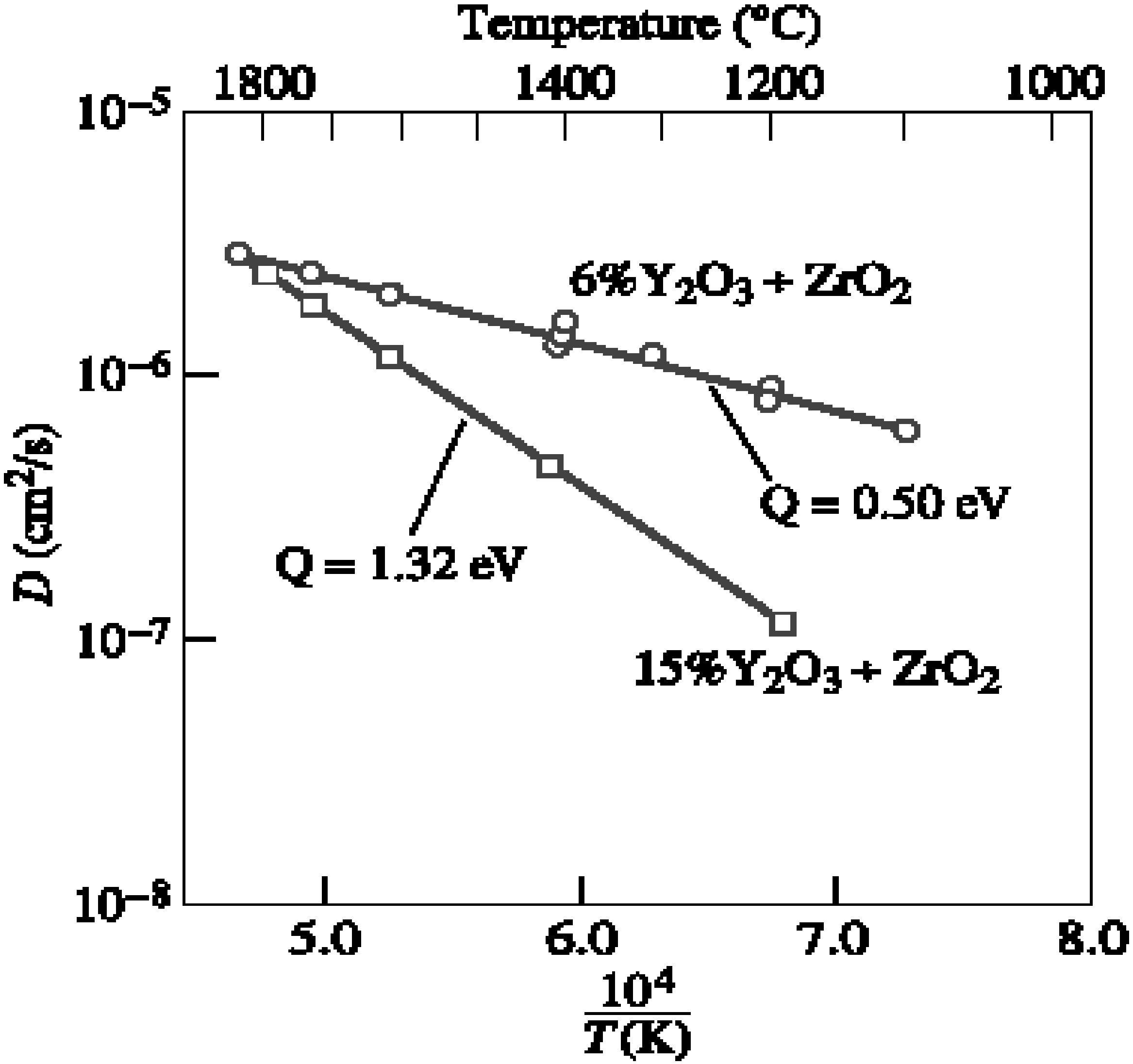
From several sources, including Adda, Y. and Philibert, J., La Diffusion dans les Solides, Vol. 2, 1966.

Factors Affecting Diffusion

- ☐ Temperature and the Diffusion Coefficient (D)
- ☐ Types of Diffusion - volume diffusion, grain boundary diffusion, Surface diffusion
- ☐ Time
- ☐ Dependence on Bonding and Crystal Structure
- ☐ Dependence on Concentration of Diffusing Species and Composition of Matrix



The diffusion coefficient *D* as a function of reciprocal temperature for some metals and ceramics. In the Arrhenius plot, *D* represents the rate of the diffusion process. A steep slope denotes a high activation energy



Diffusivity of oxygen ions in yttria stabilized zirconia ceramics

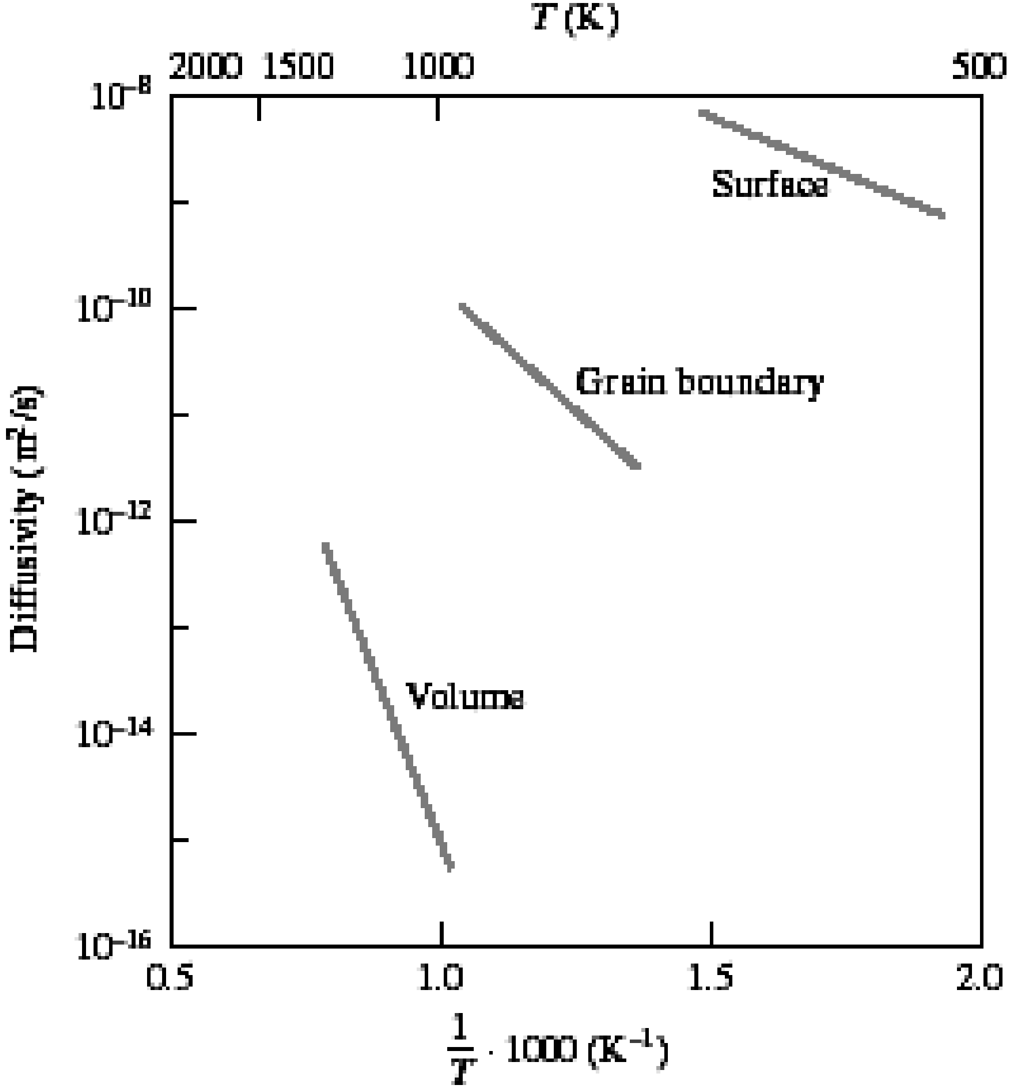
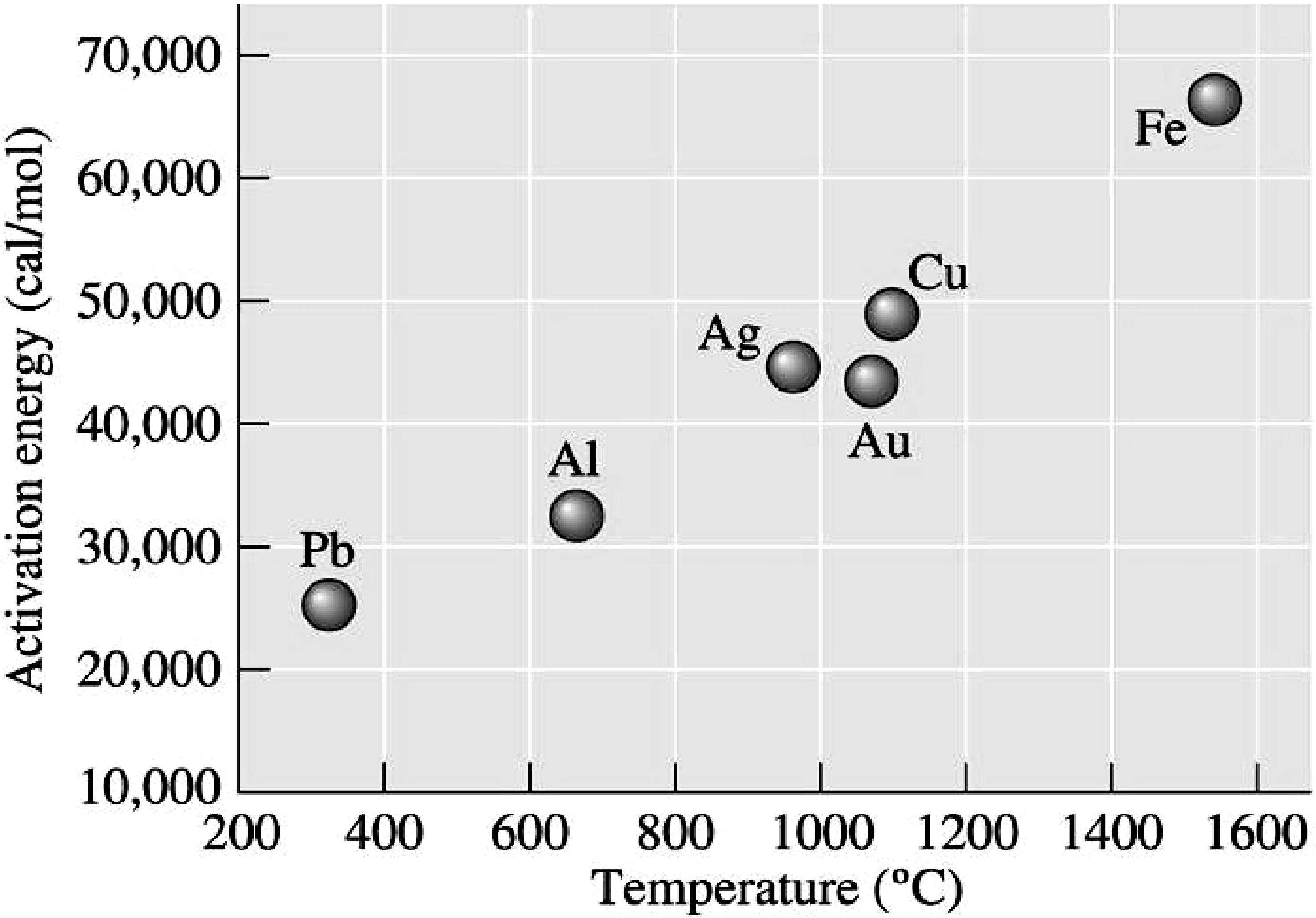


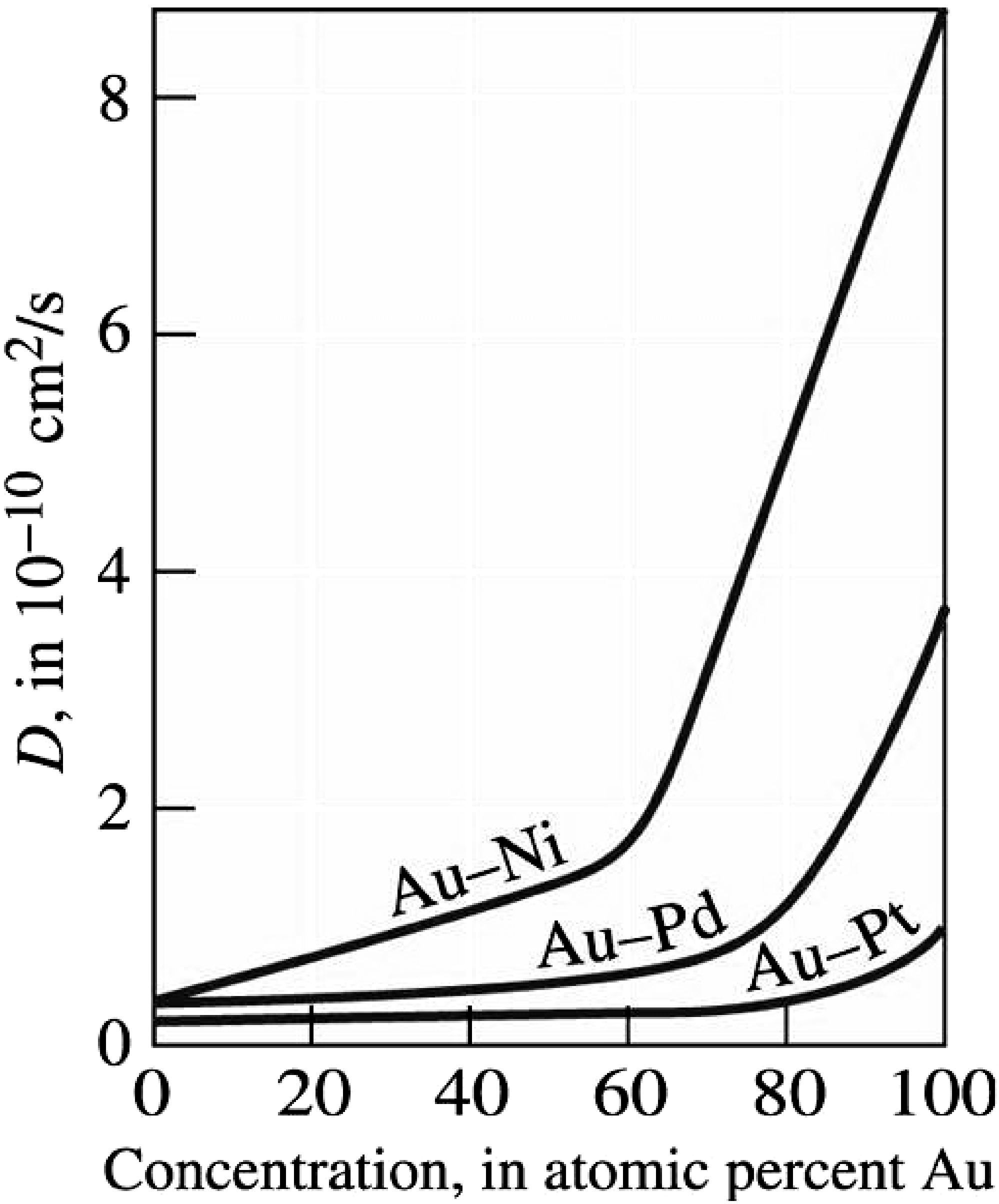
Figure 5-18 ***Self-diffusion coefficients for silver depend on the diffusion path. In general, diffusivity is greater through less restrictive structural regions (After J. H. Brophy, R. M. Rose, and J. Wulff,*** The Structure and Properties of Materials, ***Vol. 2:*** Thermodynamics of Structure, ***John Wiley & Sons, Inc., New York, 1964.)***

As one would expect, the diffusion coefficient is lowest for volume diffusion and orders of magnitude reduced for diffusion at places where atoms are less tightly bound

In addition, note the strong dependency of the diffusion coefficient (diffusivity) on the temperature



Activation energy for self-diffusion increases as the melting point of the metal increases, so that is another property that depends on the strength of the bonds



dependence of diffusion coefficient of Au on concentration, *so things can be quite complicated*

Composition Profile (Fick's Second Law)

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}(D\frac{\partial c}{\partial x})$$

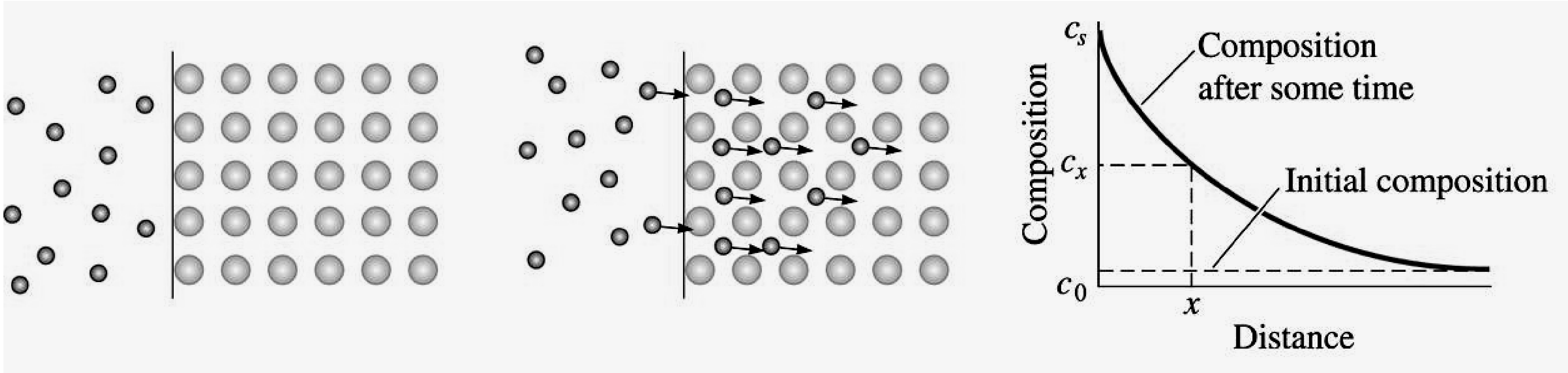
The partial differential equation that describes the rate at which atoms are redistributed in a material by diffusion. If we assume that diffusion coefficient D is not a function of location x and the concentration of diffusing species (starting boundary conditions), we can simplify

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$

One important solution is:

$$\frac{c_s - c_x}{c_s - c_o} = erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

Diffusion of atoms into the surface of a material illustrating the use of Fick's second law, c_s is constant concentration of the diffusing atom at the surface of a material, c_0 is that atoms initial concentration in the material, and c_x is that atoms concentration at location x below the surface at time t



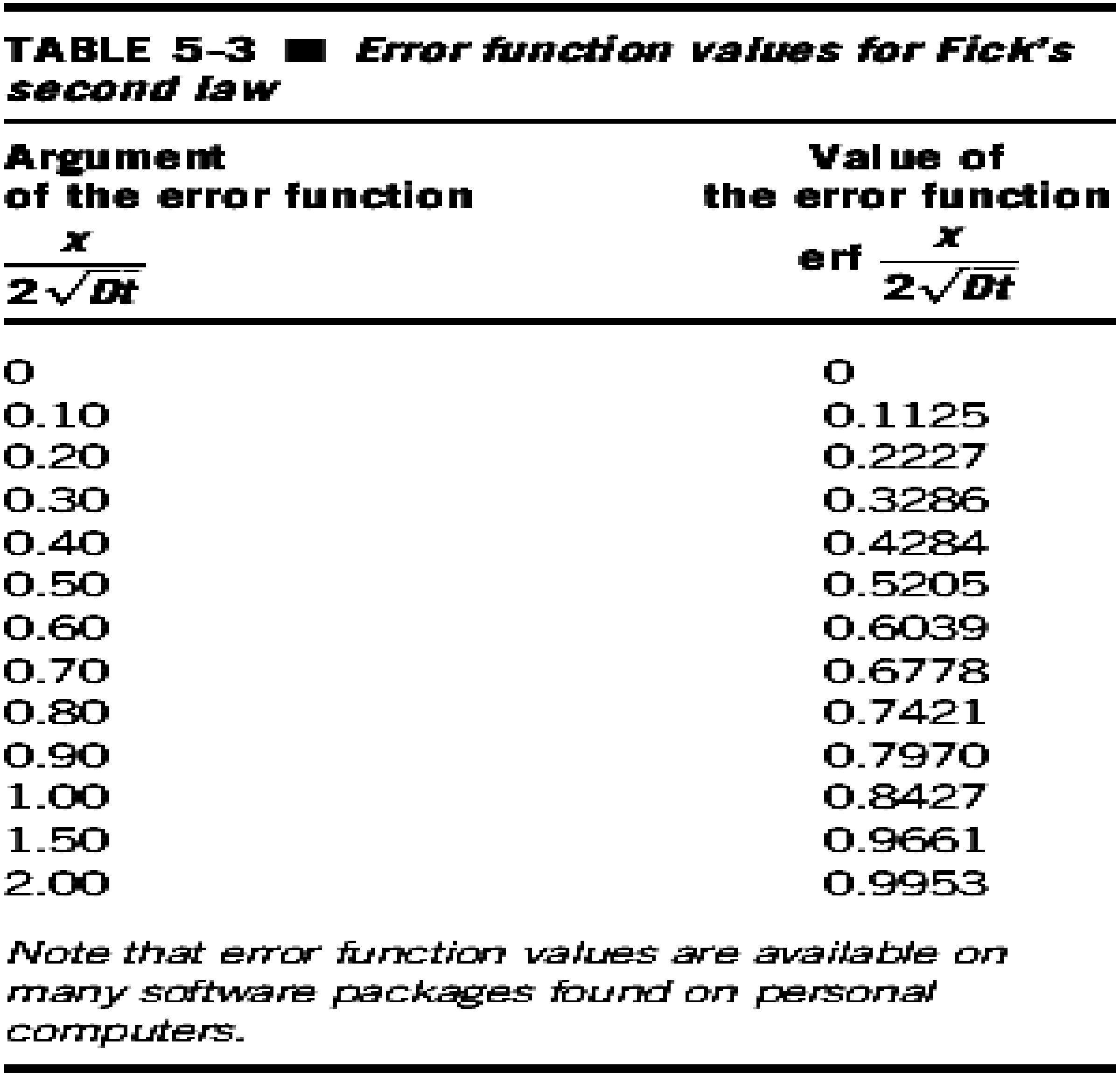
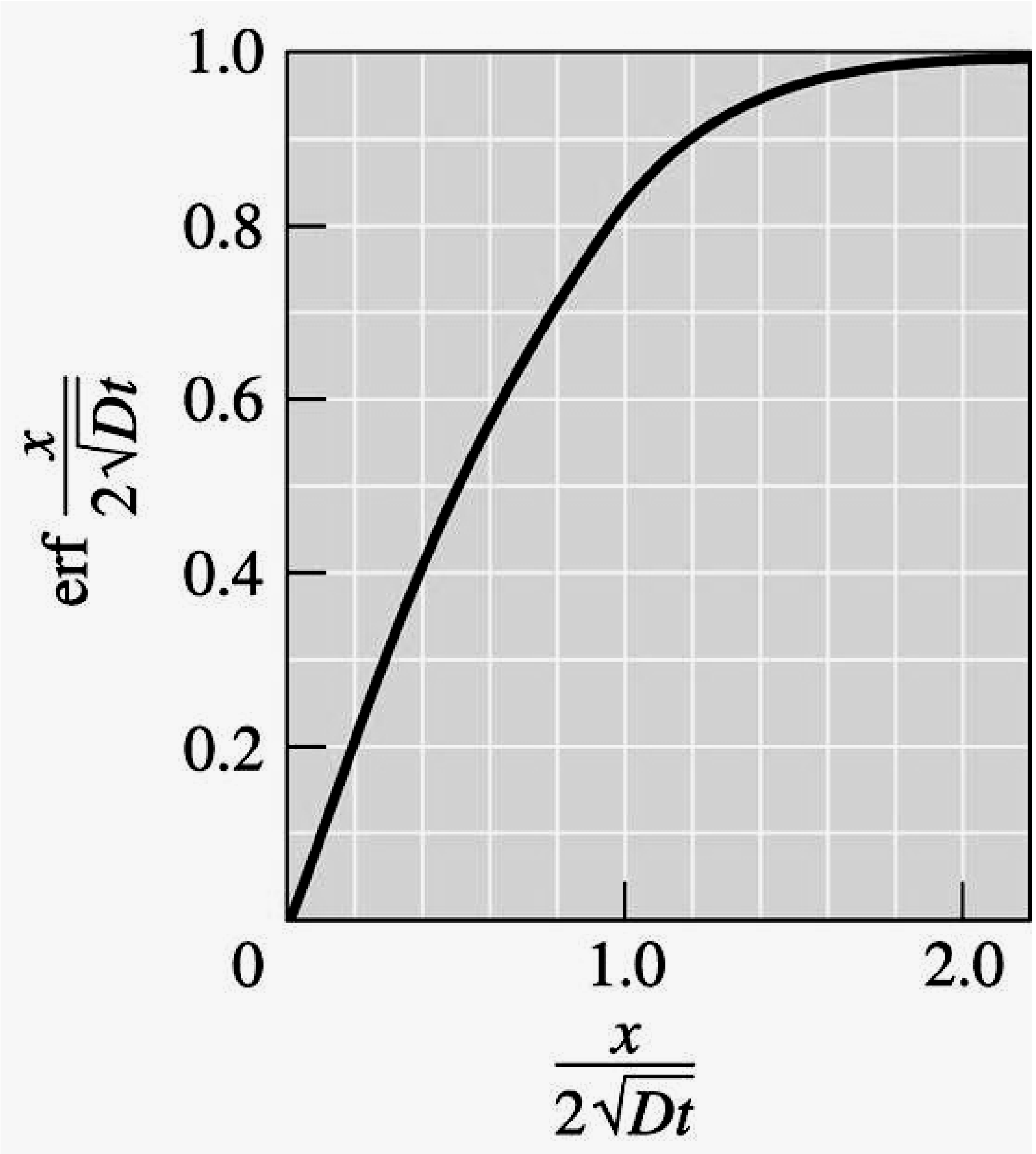


TABLE 5–3 ■ ***Error function values for Fick's second law***

Argument of the error function $\frac{x}{2\sqrt{Dt}}$	Value of the error function $\operatorname{erf} \frac{x}{2\sqrt{Dt}}$
0	0
0.10	0.1125
0.20	0.2227
0.30	0.3286
0.40	0.4284
0.50	0.5205
0.60	0.6039
0.70	0.6778
0.80	0.7421
0.90	0.7970
1.00	0.8427
1.50	0.9661
2.00	0.9953

Note that error function values are available on many software packages found on personal computers.



Graph showing the argument and value of error function encountered in Fick’s second law

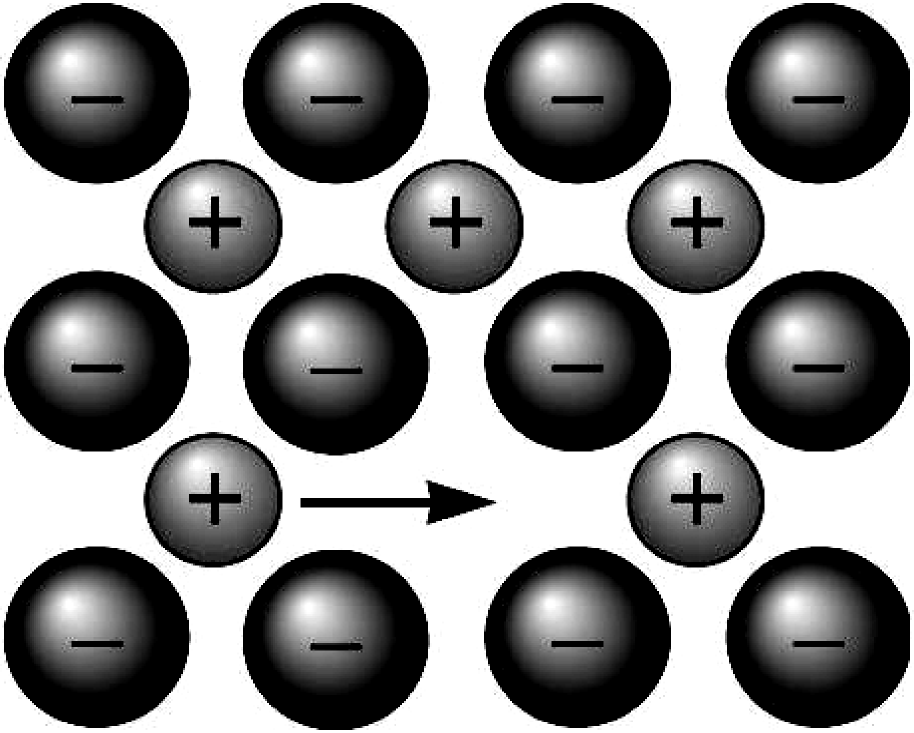
energy & diffusion

Diffusion FASTER for…	Diffusion SLOWER for…
• open crystal structures	• close-packed structures
• lower melting T materials	• higher melting T materials
• materials w/secondary bonding	• materials w/covalent bonding
• smaller diffusing atoms	• larger diffusing atoms
• cations	• anions
• lower density materials	• higher density materials

summary: structure & diffusion

Diffusion FASTER for…	**Diffusion SLOWER for…**
• open crystal structures	• close-packed structures
• lower melting T materials	• higher melting T materials
• materials w/secondary bonding	• materials w/covalent bonding
• smaller diffusing atoms	• larger diffusing atoms
• cations	• anions
• lower density materials	• higher density materials

Electric conductivity and diffusion, this law must be expressed by an Arrhenius equation as well



Diffusion in ionic compounds. Anions can only enter other anion sites. Smaller cations tend to diffuse faster

Dislocations

- ☐ Dislocation - A line imperfection in a crystalline material.
- ☐ Screw dislocation - A dislocation resulting from complicated processes it “looks like” a spiral ramp about the dislocation in the plane perpendicular to it
- ☐ Edge dislocation - A dislocation resulting from complicated processes it “looks like” an ‘‘extra half plane’’ of atoms.
- ☐ Mixed dislocation - A dislocation that contains partly edge components and partly screw components.
- ☐ Slip – Plastic, i.e. permanent, deformation of a metallic material by the movement of dislocations through the crystal.

- **dislocations are line defects,**
- **slip of one plane of atoms over another plane of atoms equivalent to their movement**
- **produce permanent (plastic) deformation.**

- **before deformation**

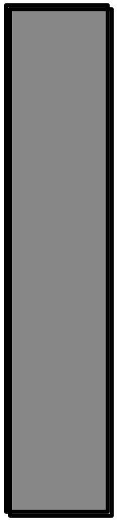
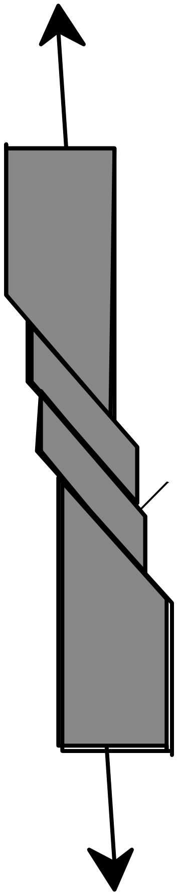


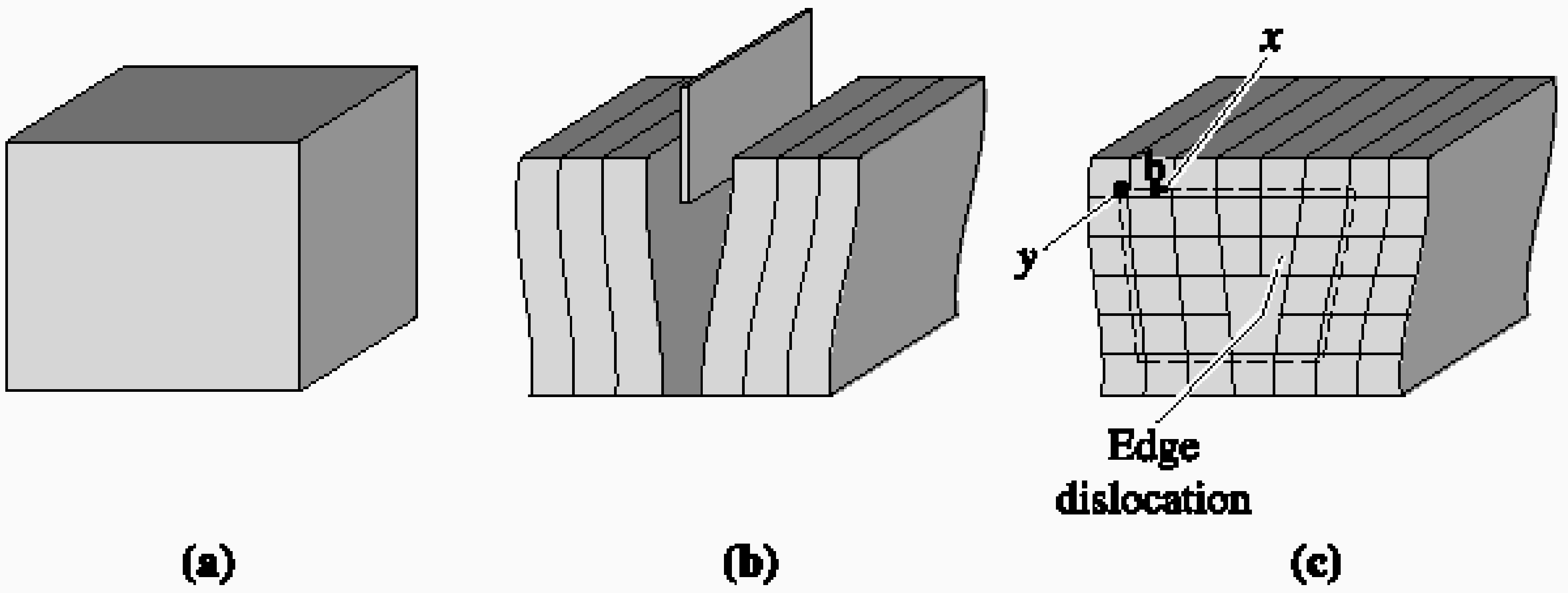
Figure 6-7 *Neck down of a tensile test specimen within its gage length after extension beyond the tensile strength. (Courtesy of R. S. Wortman)*

- **after tensile elongation**

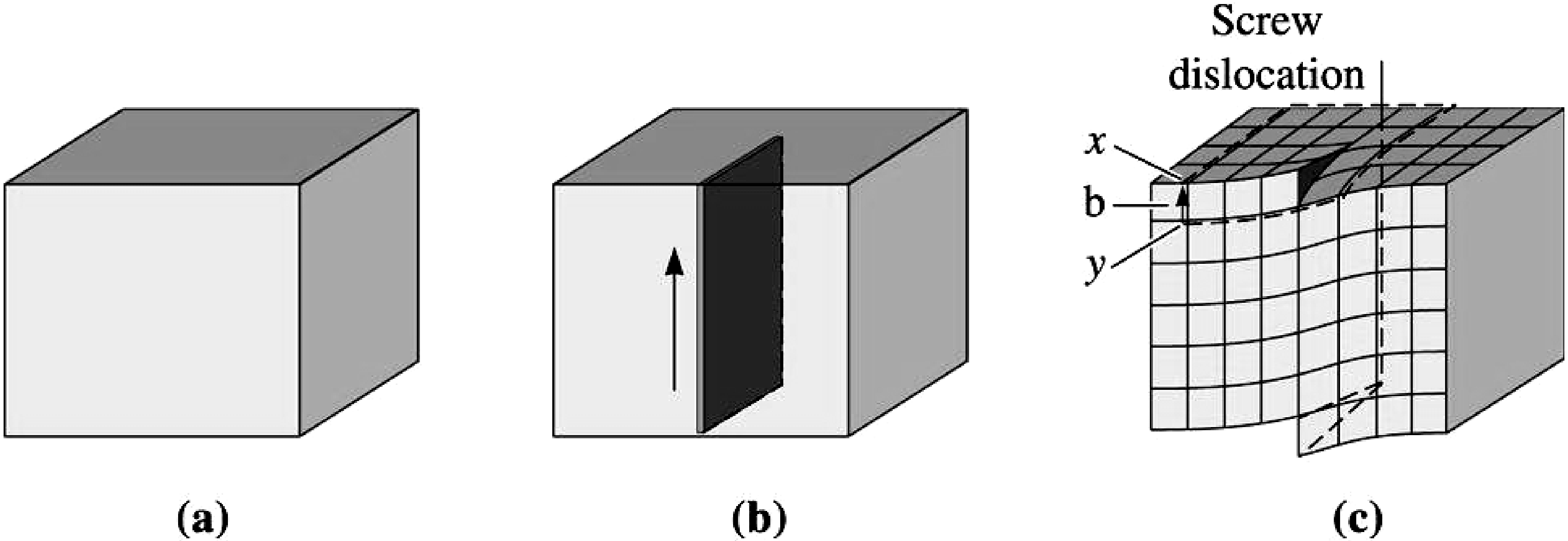


slip steps

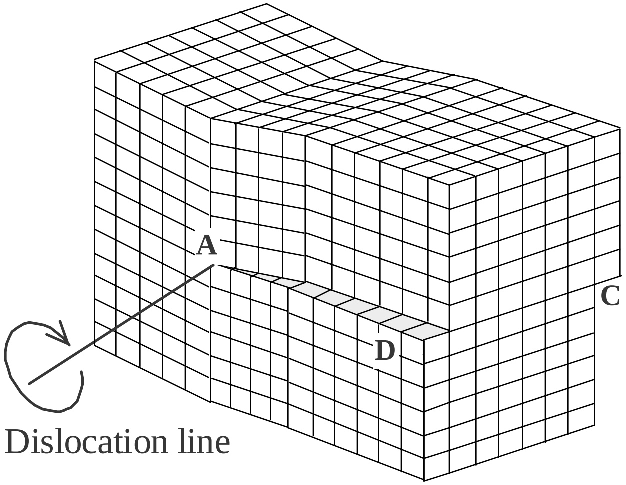
Schematic of a Zinc single crystal, HCP-structure



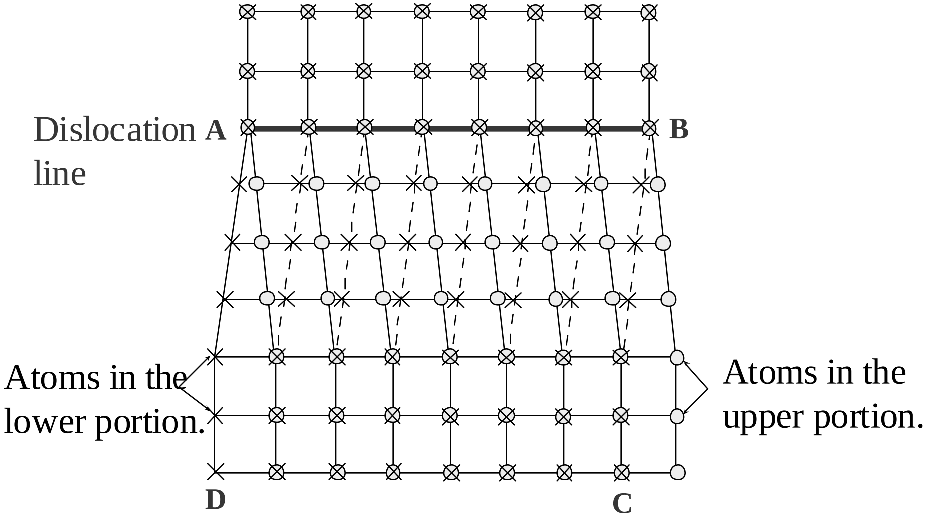
In order to make up a model of an edge dislocation: perfect crystal in (a) is cut and an extra plane of atoms is inserted (b). The bottom edge of the extra plane is the edge dislocation (c). The Burgers vector b closes the loop of equal atom spacings around the edge dislocation.



In order to make up a model of a screw dislocation: perfect crystal (a) is cut and sheared one atom spacing, (b) and (c). The line along which shearing occurs is the screw dislocation. The Burgers vector *b* of the dislocation closes the loop of equal atom spacings around the screw dislocation.

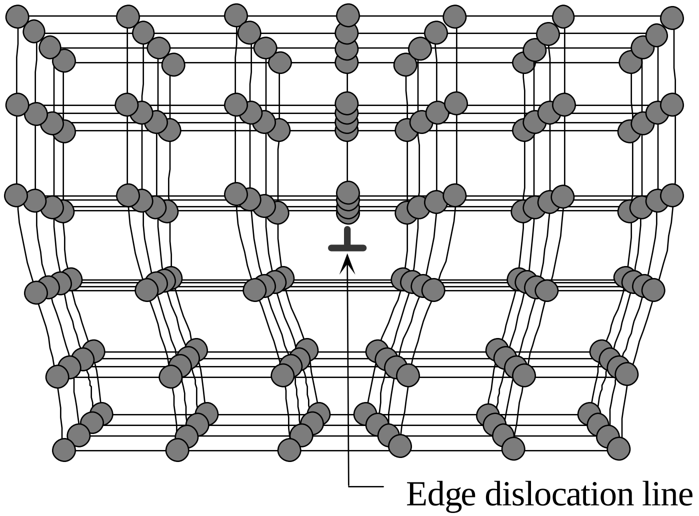


(a) A screw dislocation in a crystal.

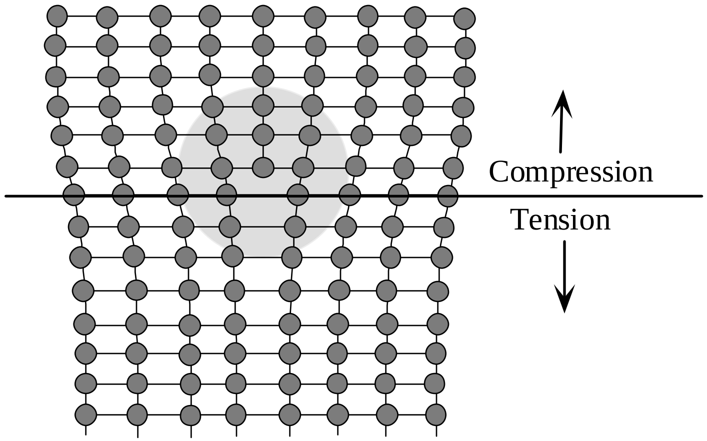


(b) The screw dislocation in (a) as viewed from above.

Fig. 1.47: A screw dislocation involves shearing one portion of a perfect crystal with respect to another portion on one side of a line (AB).



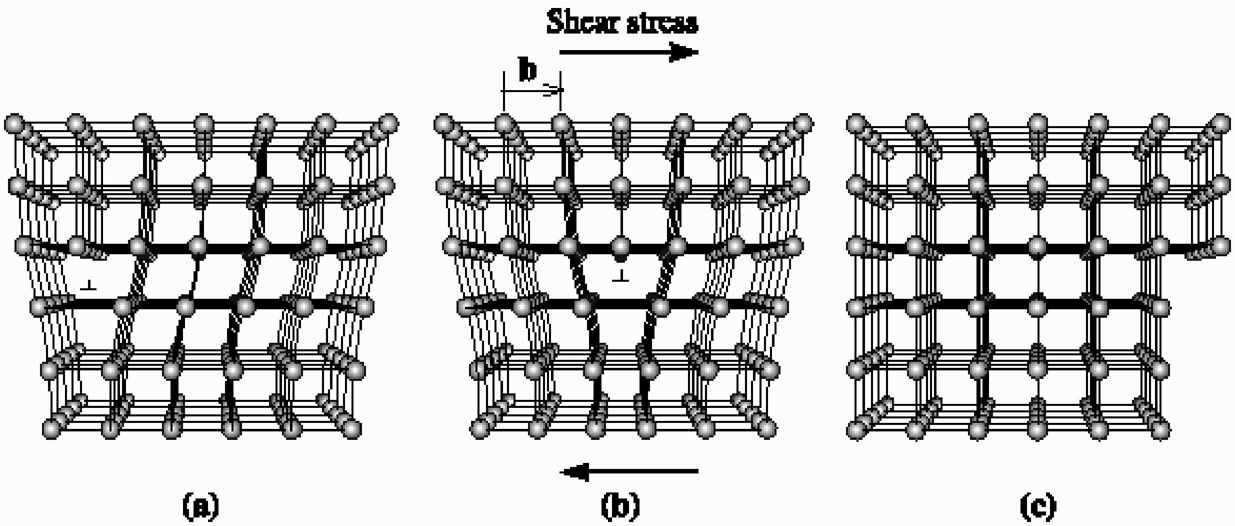
(a) Dislocation is a line defect. The dislocation shown runs into the paper.

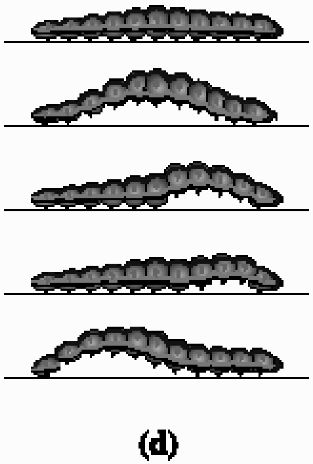


(b) Around the dislocation there is a strain field as the atomic bonds have been compressed above and stretched below the islocation line

Fig. 1.46: Dislocation in a crystal is a line defect which is accompanied by lattice distortion and hence a lattice strain around it.

Point defects in the crystal will go to the Compressive side if they are “smaller” and to the tension side if they are “larger”, it is all driven by the energy minimization principle





You can move a large carpet spread out on the ground by the same mechanism, first make a small “dislocation” on one side then push the “dislocation” trough to the other side, when the dislocation has slipped out, the carpet is moved by a bit

(a) When a shear stress is applied to the dislocation in (a), the atoms are displaced, causing the dislocation to move one Burgers vector in the slip direction (b). Continued movement of the dislocation eventually creates a step (c), and the crystal is deformed. (d) Motion of caterpillar is analogous to the motion of a dislocation.

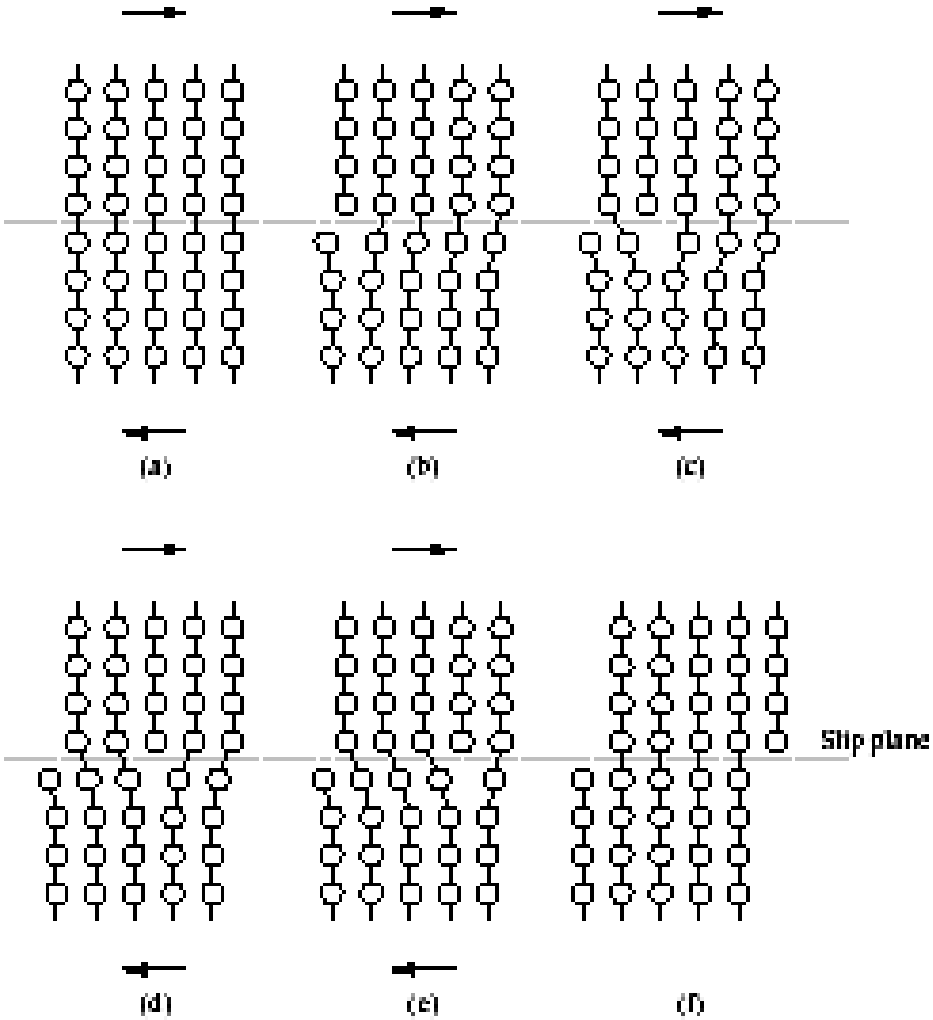


Figure 6-20 *A low-stress alternative for plastically deforming a crystal involves the motion of a dislocation along a slip plane.*

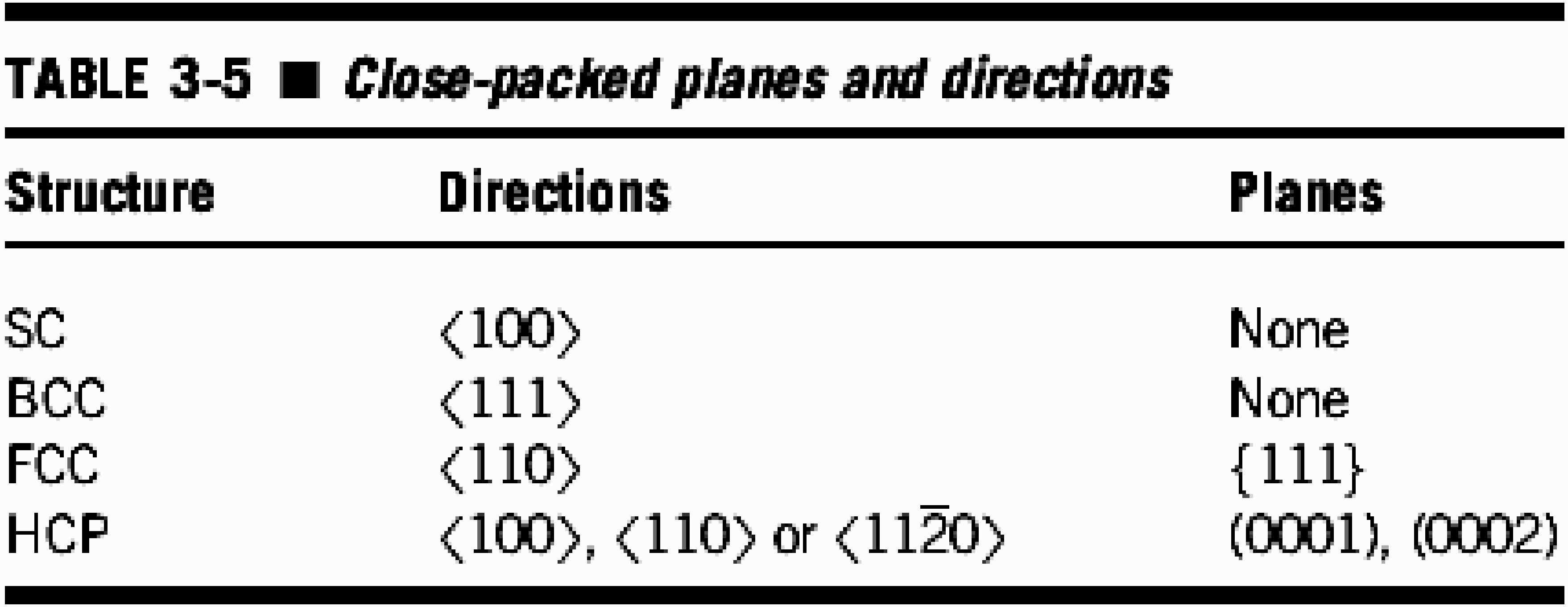


TABLE 3-5 ■ *Close-packed planes and directions*

Structure	Directions	Planes
SC	⟨100⟩	None
BCC	⟨111⟩	None
FCC	⟨110⟩	{111}
HCP	⟨100⟩, ⟨110⟩ or ⟨11$\bar{2}$0⟩	(0001), (0002)

The Burgers vector is as short as possible as it represents excess energy. Therefore it runs in the closes packed directions that lie in the closes packed planes, see above

Those directions and planes will be very important to understand plastic deformations as glide systems are combinations of close packed planes and directions, i.e. <110>/{111} in semiconductors such as Si, GaAs, ZnSe,

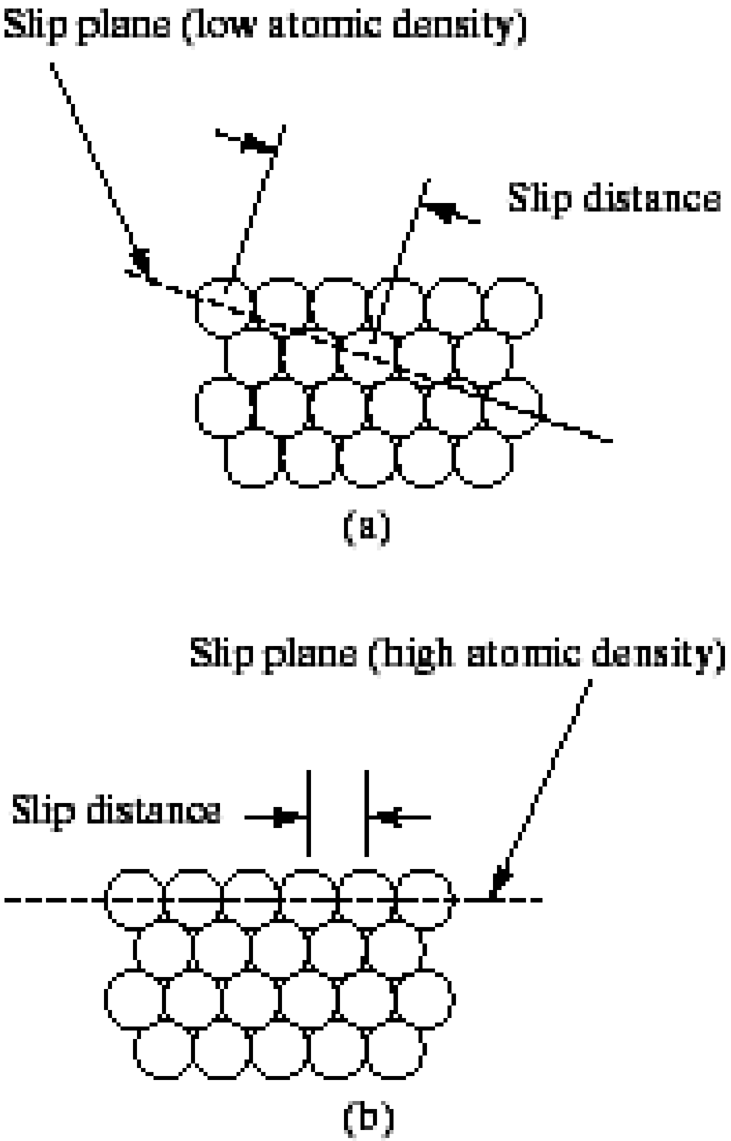
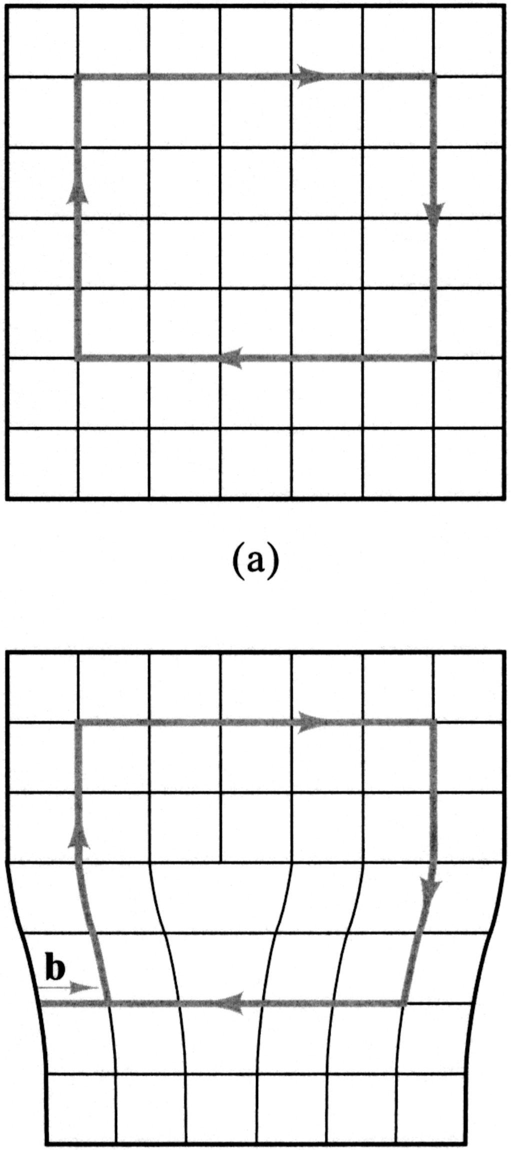


Figure 6-23 *Dislocation slip is more difficult along (a) a low-atomic-density plane than along (b) a high-atomic-density plane.*

Figure 4-11 *Definition of the Burgers vector,* **b,** *relative to an edge dislocation. (a) In the perfect crystal, an m × n atomic step loop closes at the starting point. (b) In the region of a dislocation, the same loop does not close, and the closure vector* **(b)** *represents the magnitude of the structural defect. For the edge dislocation, the Burgers vector is* perpendicular *to the dislocation line.*



(b)

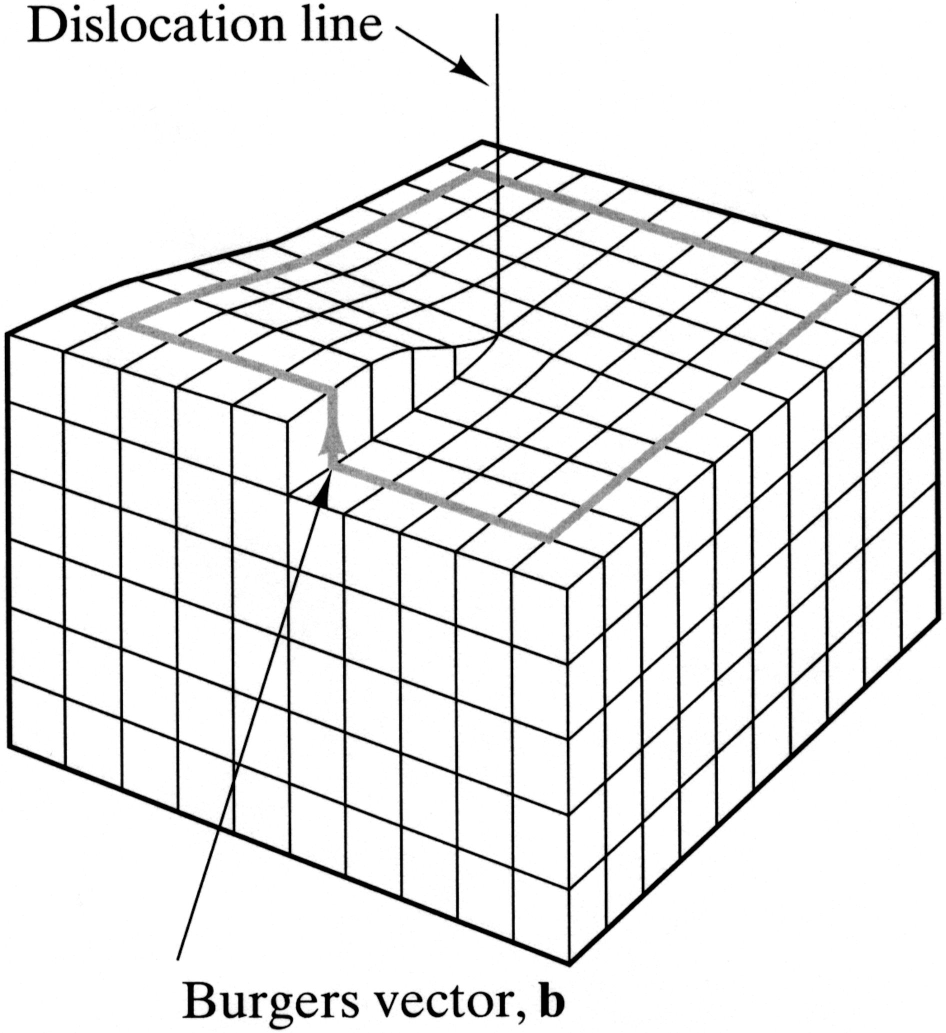
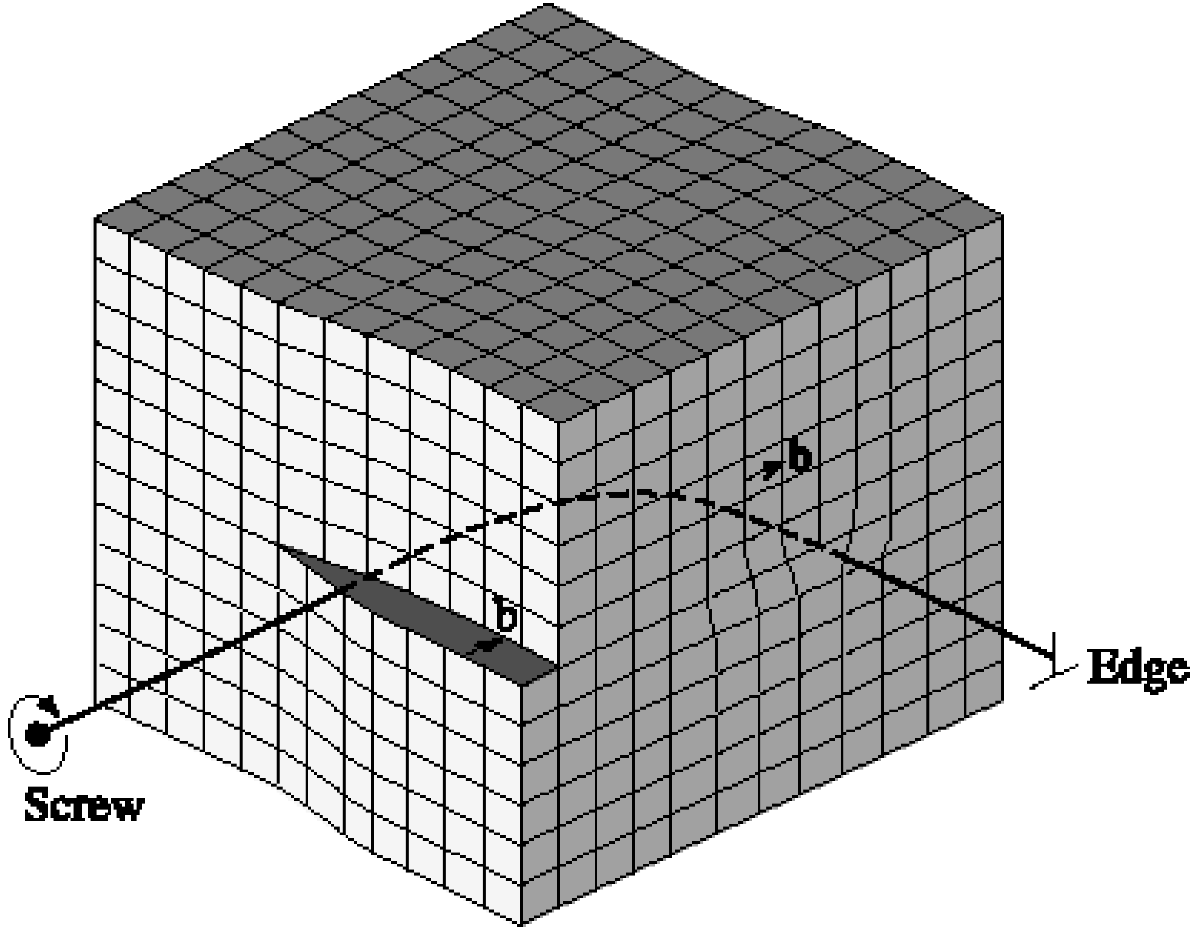


Figure 4-12 *Screw dislocation. The spiral stacking of crystal planes leads to the Burgers vector being* parallel *to the dislocation line.*



The real thing: a mixed dislocation. The screw dislocation at the front face of the crystal gradually changes to an edge dislocation at the side of the crystal. The Burgers vector remains the same at all times

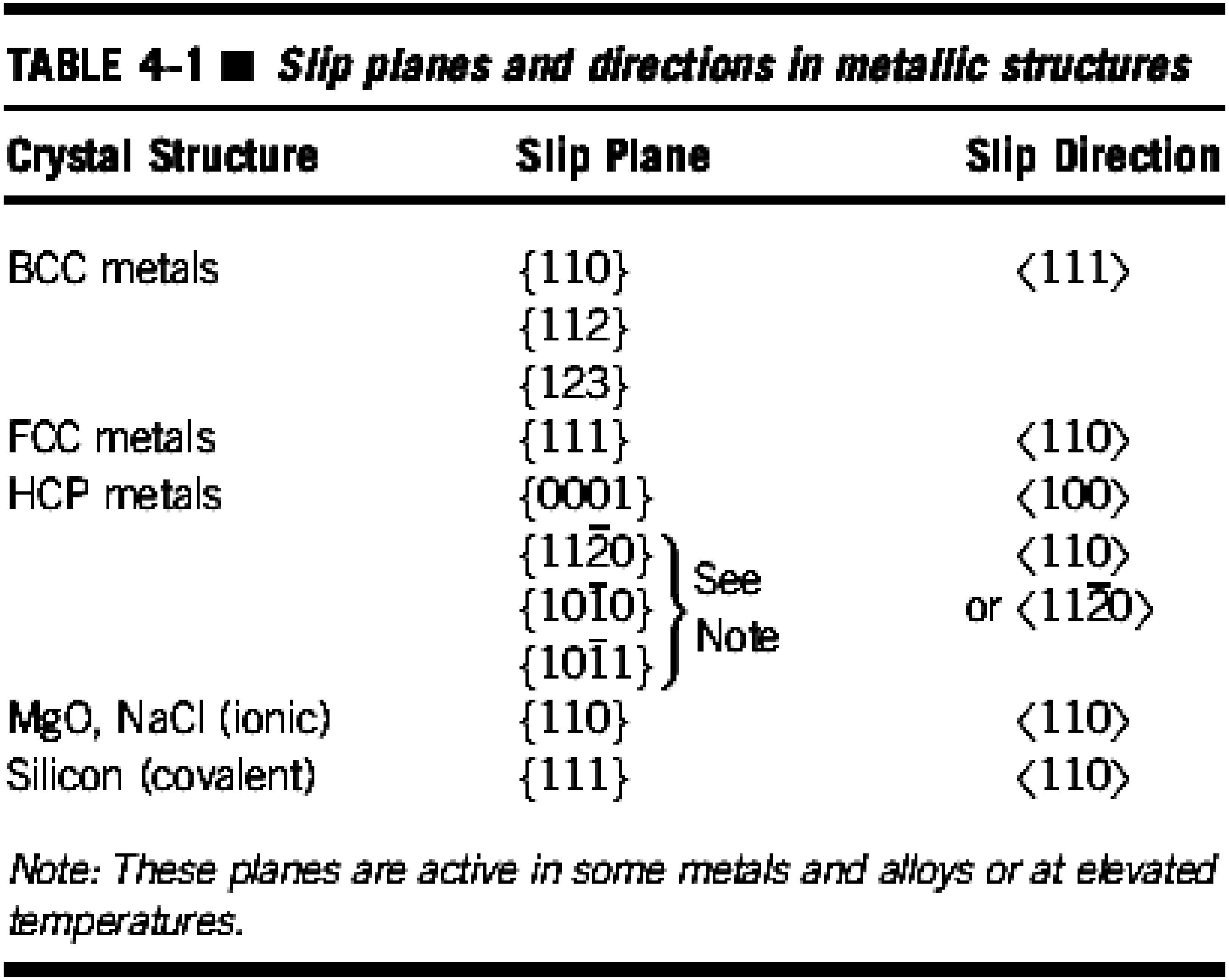


TABLE 4-1 ■ *Slip planes and directions in metallic structures*

Crystal Structure	Slip Plane	Slip Direction
BCC metals	$\{110\}$	$\langle 111\rangle$
	$\{112\}$	
	$\{123\}$	
FCC metals	$\{111\}$	$\langle 110\rangle$
HCP metals	$\{0001\}$	$\langle 100\rangle$
	$\{11\bar{2}0\}$ See Note	$\langle 110\rangle$
	$\{10\bar{1}0\}$ See Note	or $\langle 11\bar{2}0\rangle$
	$\{10\bar{1}1\}$ See Note	
MgO, NaCl (ionic)	$\{110\}$	$\langle 110\rangle$
Silicon (covalent)	$\{111\}$	$\langle 110\rangle$

Note: These planes are active in some metals and alloys or at elevated temperatures.

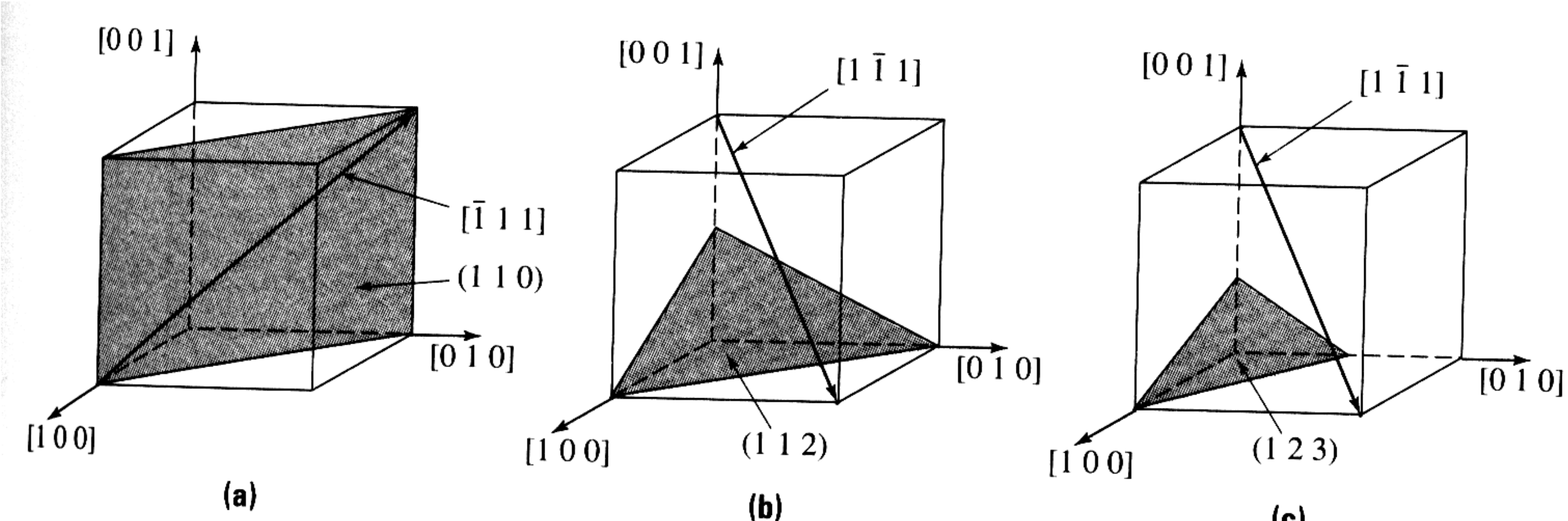
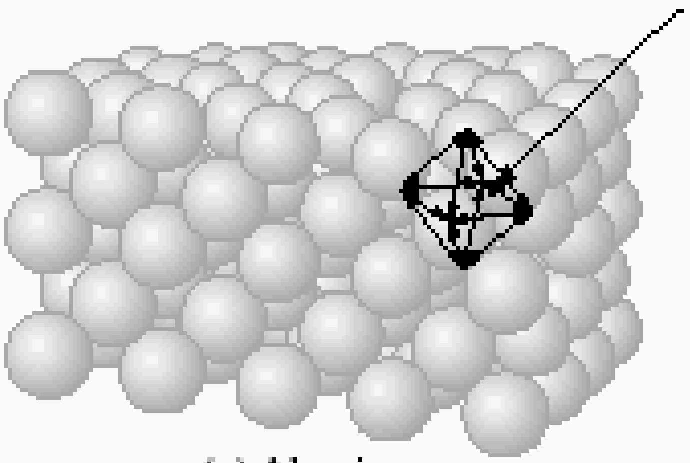


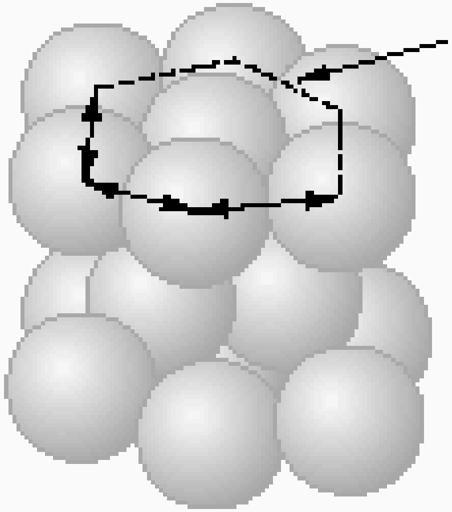
FIGURE 5.2–13 Slip planes and directions in the BCC structure: **(a)** a member of the {1 1 0}⟨1 1 1⟩ system, **(b)** a member of the {1 1 2}⟨1 1 1⟩ system, and **(c)** a member of the {1 2 3}⟨1 1 1⟩ system.



$\{111\}\langle 1\bar{1}0\rangle =$

$(111)[1\bar{1}0]$ $(111)[\bar{1}01]$ $(111)[01\bar{1}]$
$(11\bar{1})[1\bar{1}0]$ $(11\bar{1})[101]$ $(11\bar{1})[011]$
$(1\bar{1}1)[110]$ $(1\bar{1}1)[10\bar{1}]$ $(1\bar{1}1)[011]$
$(\bar{1}11)[110]$ $(\bar{1}11)[101]$ $(\bar{1}11)[01\bar{1}]$

(a) Aluminum



$(0001)\langle 11\bar{2}0\rangle =$

$(0001)[11\bar{2}0]$ $(0001[1\bar{2}10])$ $(0001)[\bar{2}110]$

(b) Magnesium

Figure 6-24 *Slip systems for (a) fcc aluminum and (b) hcp magnesium. (Compare to Figure 1–18.)*

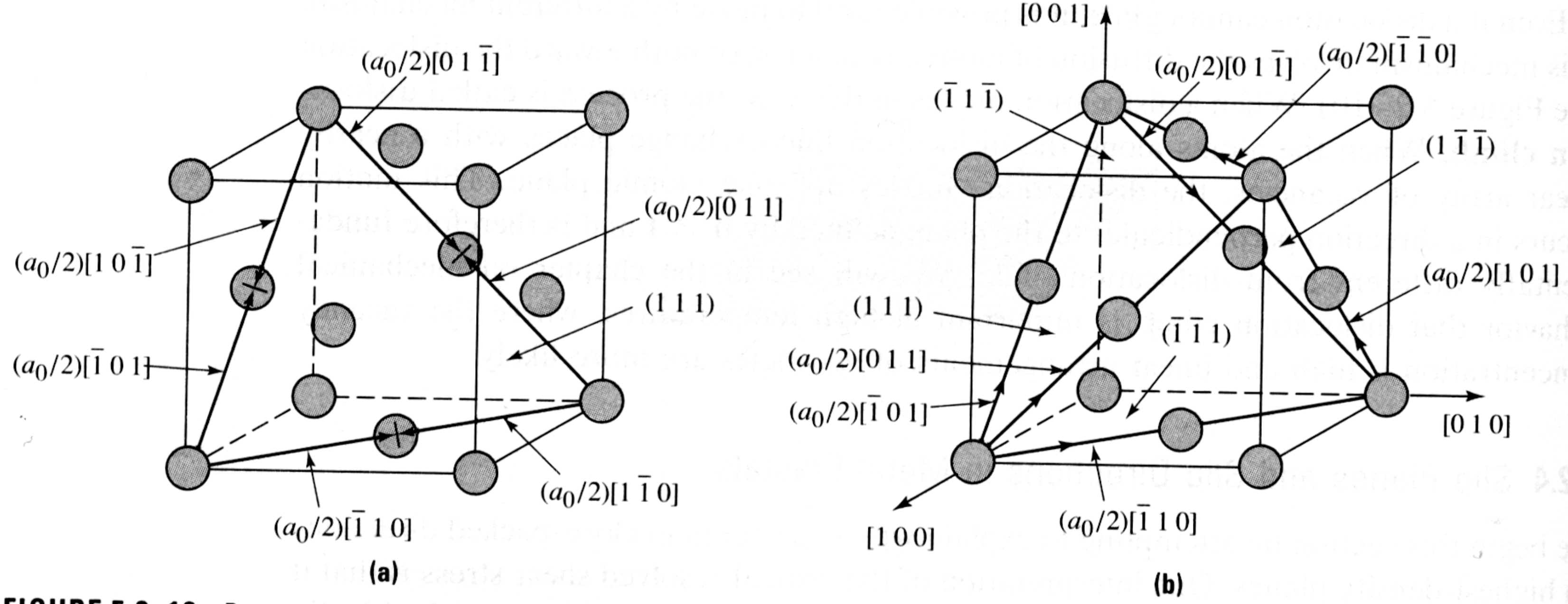
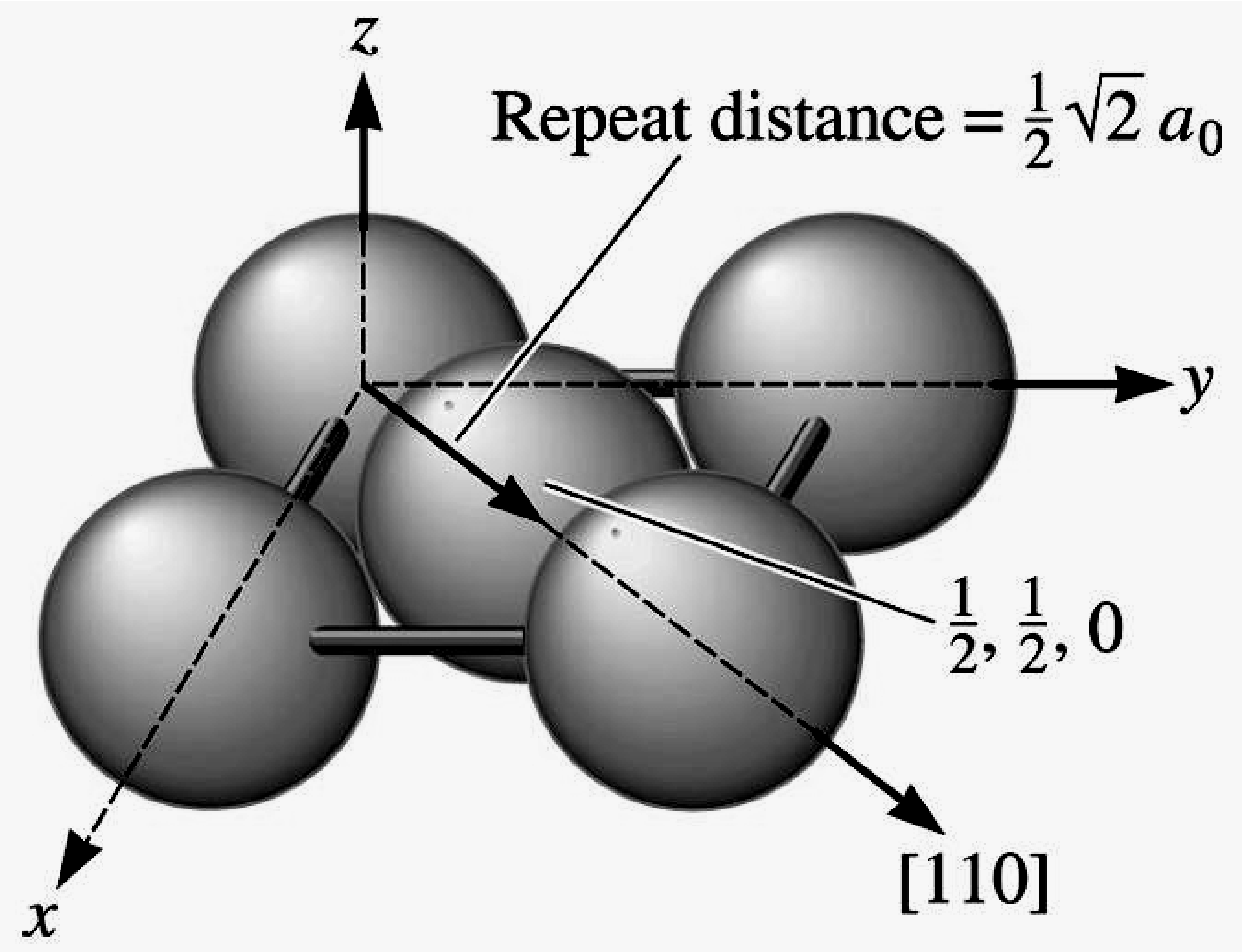


FIGURE 5.2–12 Burgers vectors and slip systems in the FCC structure: **(a)** an FCC unit cell showing the location of the (1 1 1) slip plane and the six valid Burgers vectors in the (1 1 1) plane. Note that the Burgers vectors occur in pairs, such that only three of the Burgers vectors are independent. **(b)** The tetrahedron formed by four members of the {1 1 1} family of planes in the FCC structure, including the three independent Burgers vectors in each plane.



Repeat distance is direction of highest linear density of lattice points or atoms

For FCC e.g. copper, it is $^1/_2$<110>, this will be the direction in which plastic deformation proceeds by dislocation slip, (glide)

This will therefore be the Burgers vector for a crystal with one atom per lattice point

Calculate the length of the Burgers vector in copper.

SOLUTION

Copper has an FCC crystal structure. The lattice parameter of copper (Cu) is 0.36151 nm. The close-packed directions, or the directions of the Burgers vector, are of the form $\langle 110 \rangle$. The repeat distance along the $\langle 110 \rangle$ directions is one-half the face diagonal, since lattice points are located at corners and centers of faces.

$$\text{Face diagonal} = \sqrt{2}a_0 = (\sqrt{2})(0.36151) = 0.51125 \text{ nm}$$

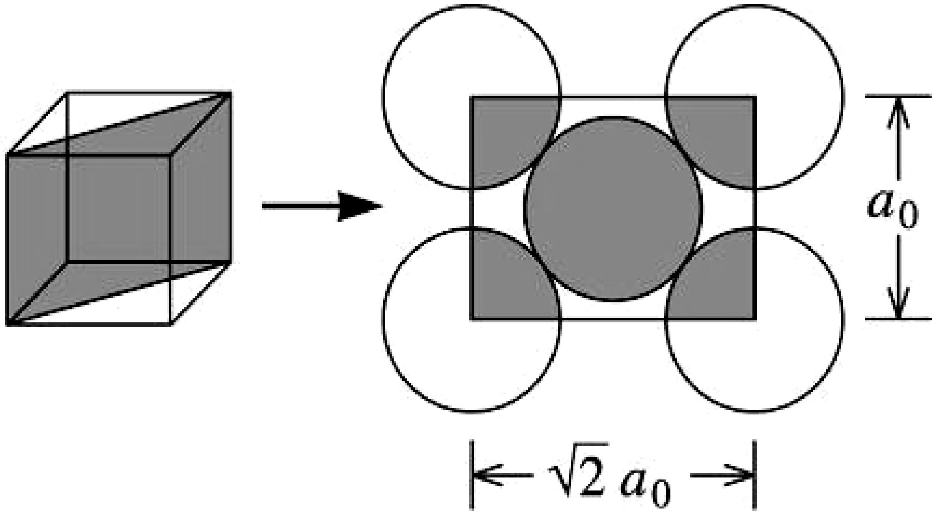
The length of the Burgers vector, or the repeat distance, is:

$$b = {}^{1}/_{2}\ (0.51125 \text{ nm}) = 0.25563 \text{ nm}$$

Identification of Preferred Slip Planes

The planar density of the (112) plane in BCC iron is 9.94 × 10^{14} atoms/cm^2, the lattice constant is 0.2886 nm

Calculate (1) the planar density of the (110) plane, Slip planes are densely packed, so on which of these two plane will slip normally occur?



The atom locations on a (110) plane in a BCC unit cell

SOLUTION

The planar density is:

$$\text{Planar density (110)} = \frac{\text{atoms}}{\text{area}} = \frac{2}{(\sqrt{2})(2.866 \times 10^{-8}\ \text{cm})^2}$$

$$= 1.72 \times 10^{15}\ \text{atoms/cm}^2$$

$$\text{Planar density (112)} = 0.994 \times 10^{15}\ \text{atoms/cm}^2\ \text{(from problem statement)}$$

The planar density of the (110) plane is larger than that of the (112) plane; therefore, the (110) plane would be the preferred slip plane.

Observing Dislocations

- Etch pits - Tiny holes created at areas where dislocations meet the surface. These are used to examine the presence and number density of dislocations.
- Slip line - A visible line produced at the surface of a metallic material by the presence of several thousand dislocations.
- Slip band - Collection of many slip lines, often easily visible.

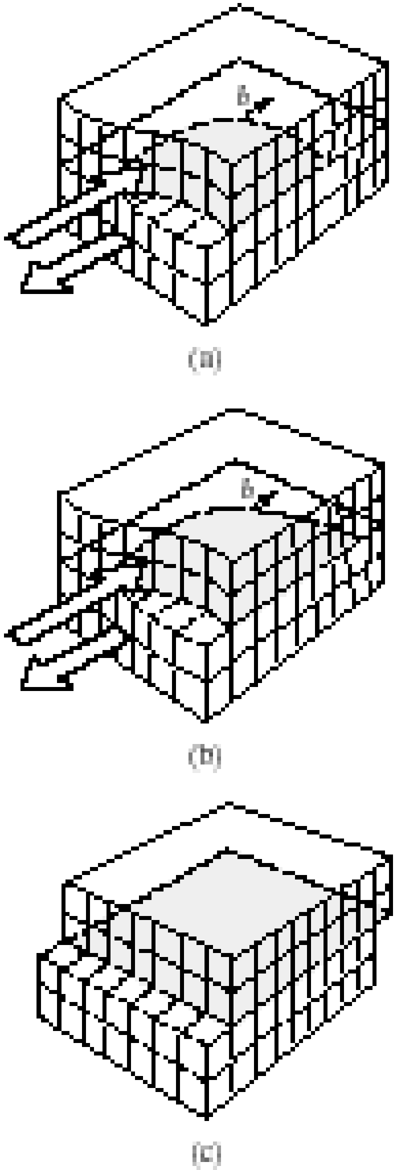
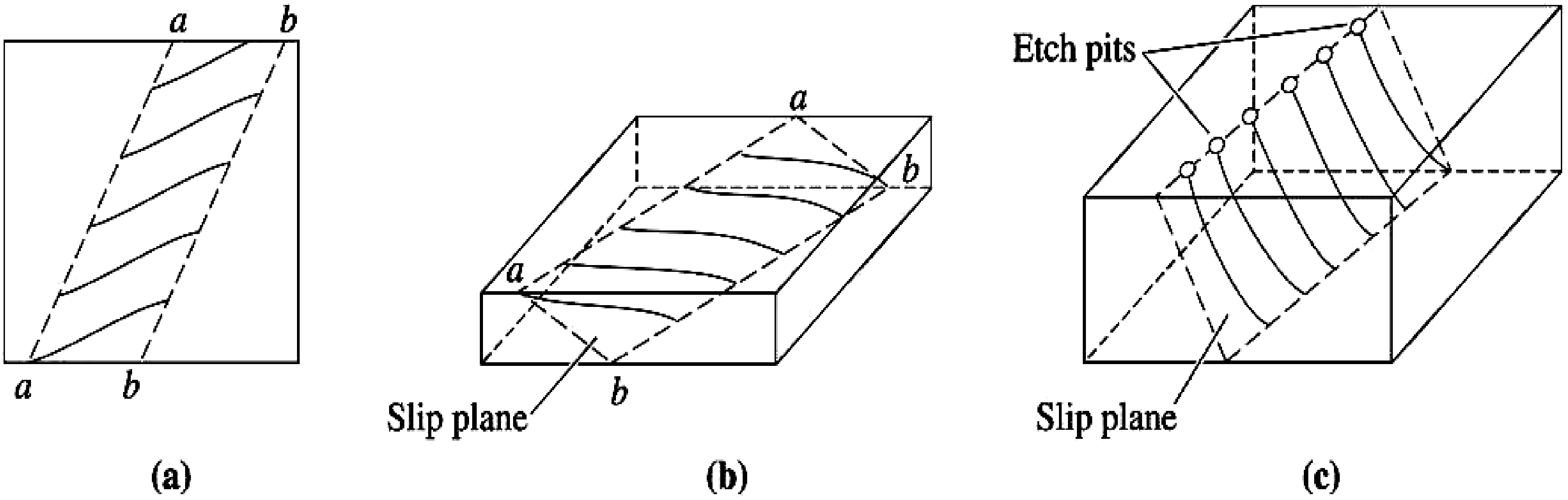
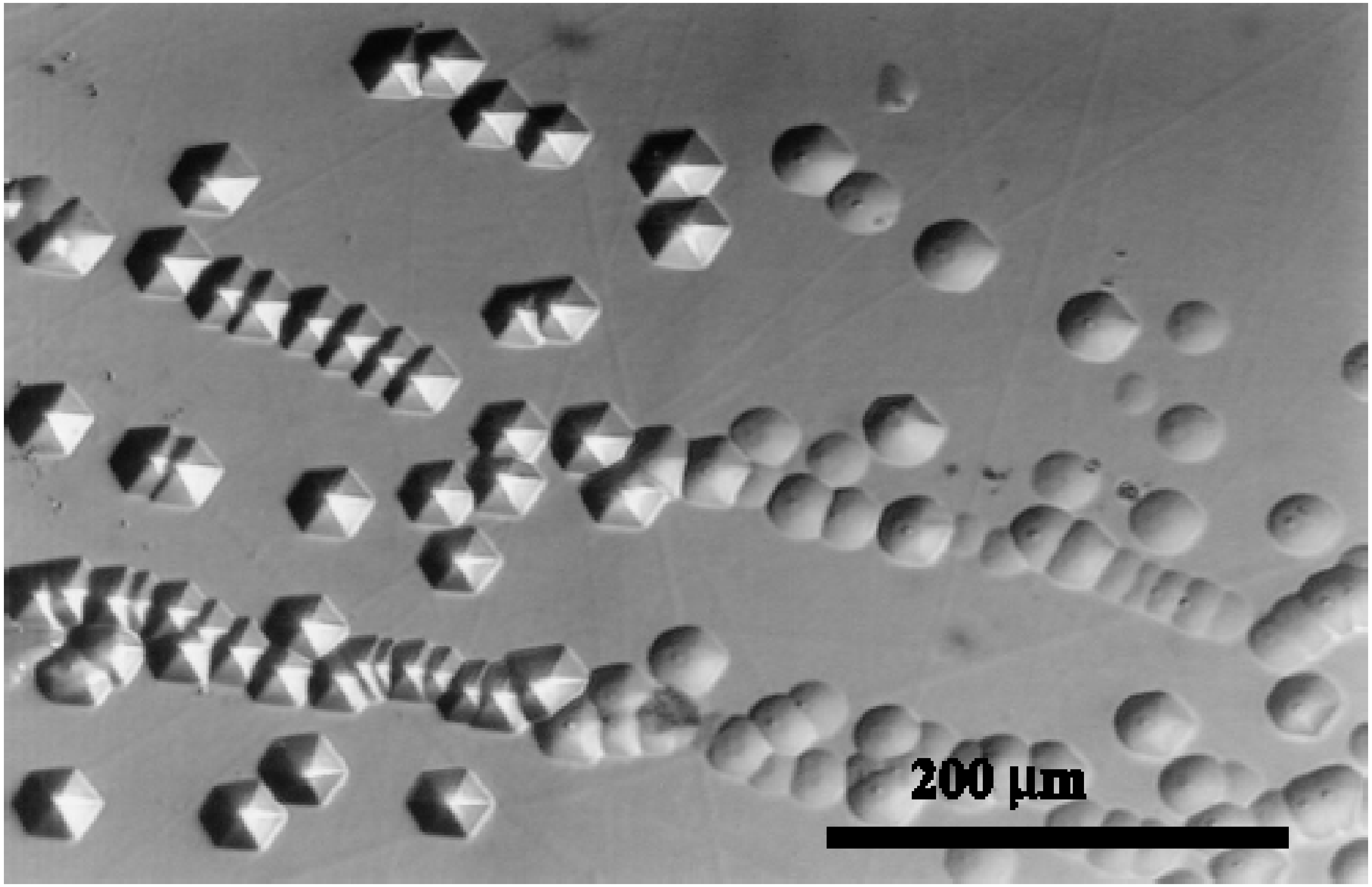


Figure 6-21 *Schematic illustration of the motion of a dislocation under the influence of a shear stress. The net effect is an increment of plastic (permanent) deformation. (Compare Figure 6–21a with Figure 4–13.)*

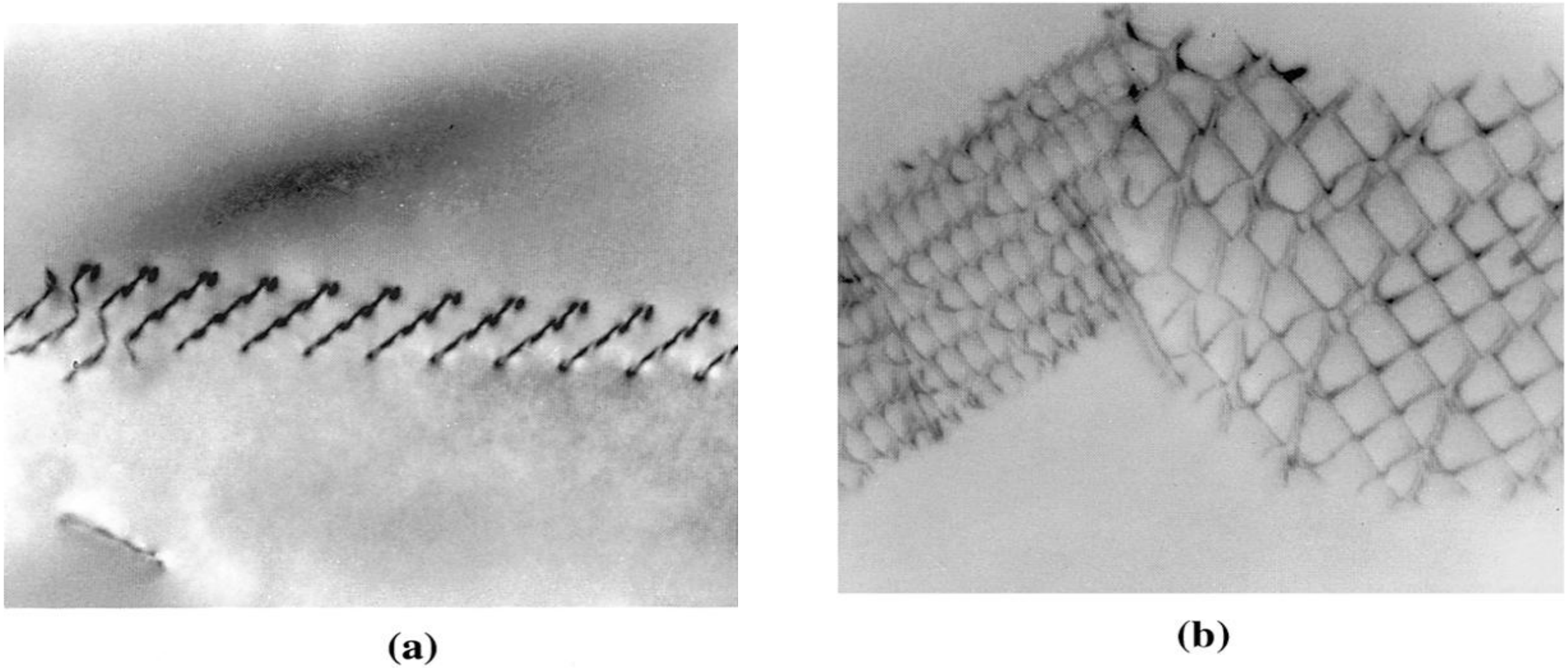
When a dislocation has glided out, a surface step remains



A sketch illustrating (a) dislocations, (b) slip planes, and (c) etch pit locations.



Optical image of etch pits in silicon carbide (SiC). The etch pits correspond to intersection points of pure edge dislocations with Burgers vector $a/_3 \langle 1\bar{1}20\rangle$ and the dislocation line direction along [0001] (perpendicular to the etched surface). Lines of etch pits represent low angle grain boundaries



Electron micrograph of dislocations in *Ti_3Al*: (a) Dislocation pileups (x 26,500). (b) Electron micrograph x 1000 showing slip lines and grain boundaries in Al.

Significance of Dislocations

- ☐ Plastic deformation refers to irreversible deformation or change in shape that occurs when the force or stress that caused it is removed.
- ☐ Elastic deformation - Deformation that is fully recovered when the stress causing it is removed.
- ☐ Dislocation density - The total length of dislocation line per cubic centimeter in a material.
- ☐ Crystal growth

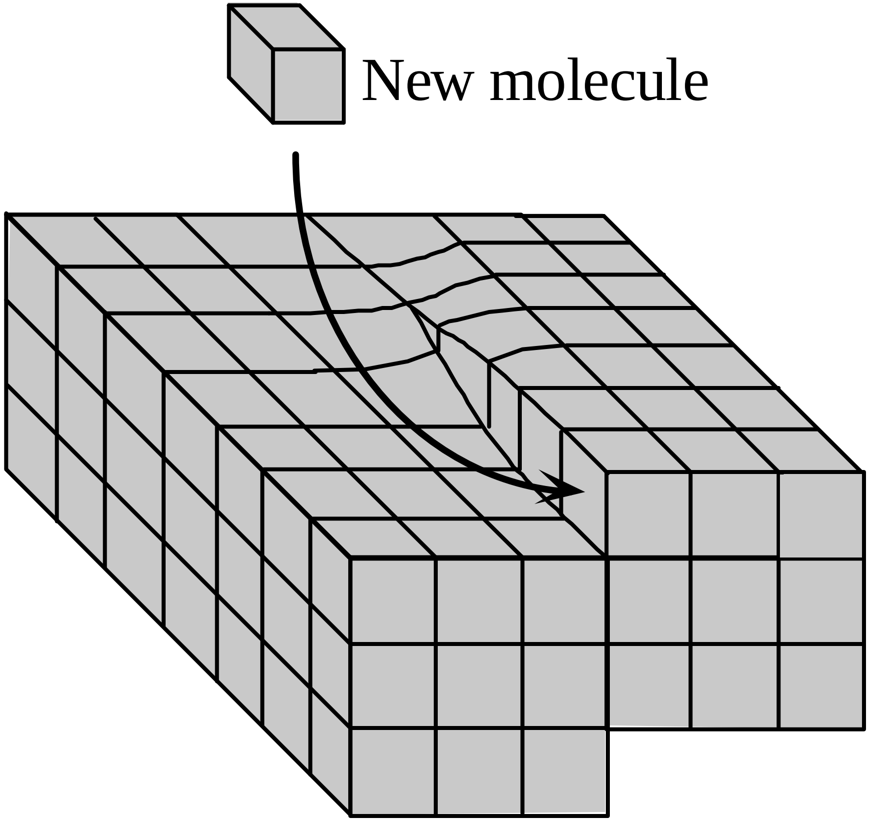


Fig. 1.49: Screw dislocation aids crystal growth because the newly arriving atom can attach to two or three atoms instead of one atom and thereby form more bonds.

Figure 5.3.2

t/a Schaffer: The Science and Design of Engineering Materials, 2/e

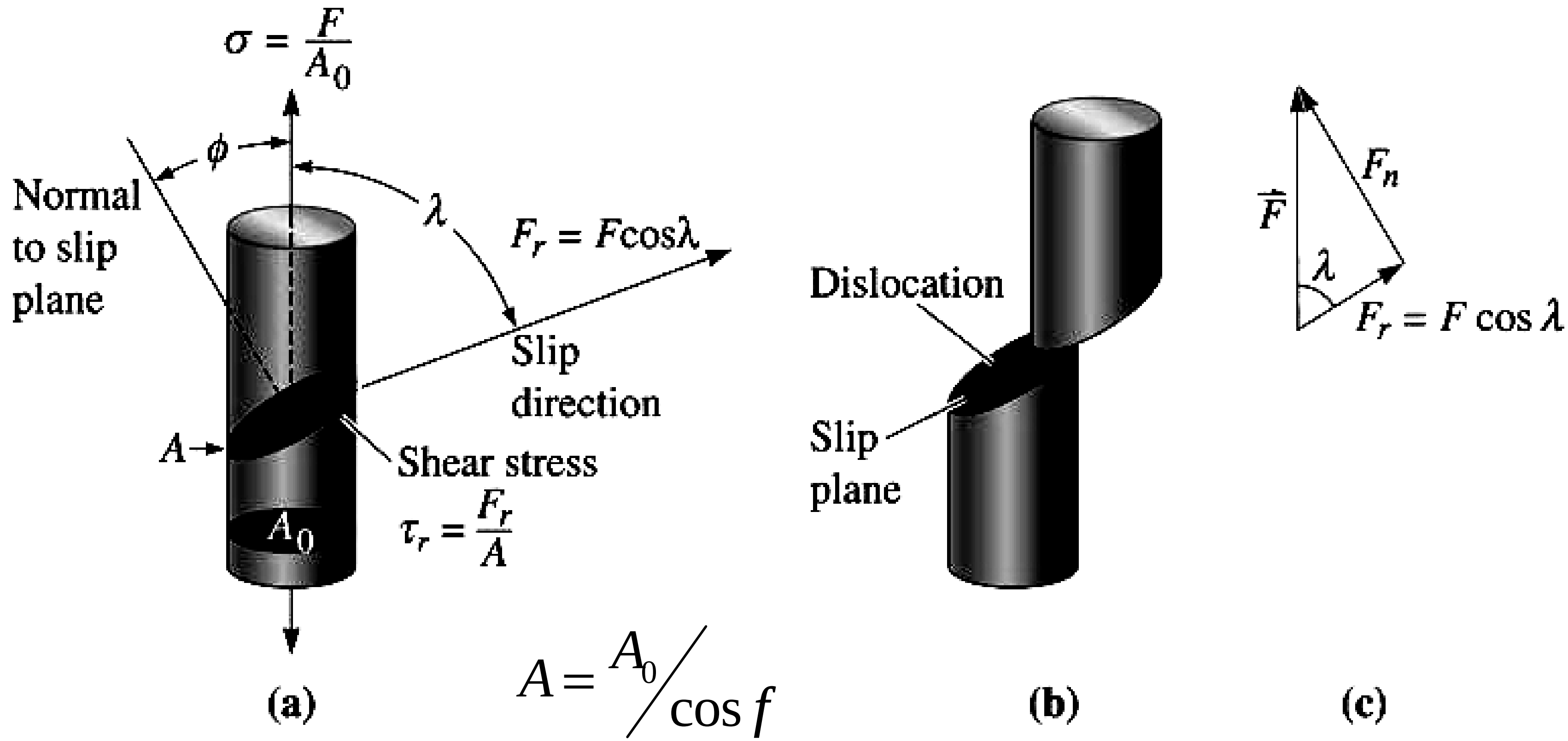
Schmid’s Law

- Schmid’s law -The relationship between shear stress, the applied stress, and the orientation of the slip system—that is,

$$t = s \cos l \cos f$$

- Critical resolved shear stress - The shear stress required to cause a dislocation to move and cause slip

When Schmid’s law results in a resolved shear stress that is larger than the critical resolved shear stress in the material, plastic deformation proceeds



$$A = A_0 / \cos f$$

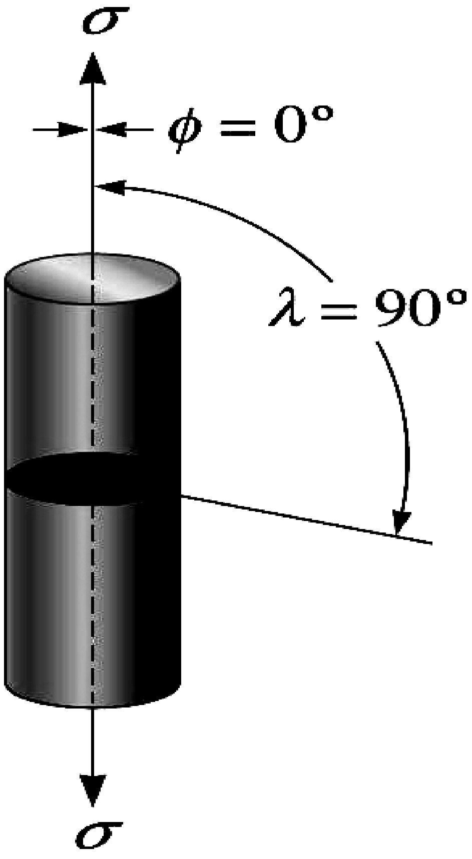
(a) A resolved shear stress t is produced on a slip system. (Note: (ø + ?) is typically not 90° (b) Movement of dislocations on the slip system deforms the material. (c) Resolving the force.

The cos l term originates from resolving / projecting the applied tensile force on the slip direction

The cos ø term originates from projecting the area on which this tensile force operates onto the slip plane

Calculation of Resolved Shear Stress

Apply the Schmid’s law for a situation in which the single crystal is at an orientation so that one of the slip planes is perpendicular to the applied tensile stress.

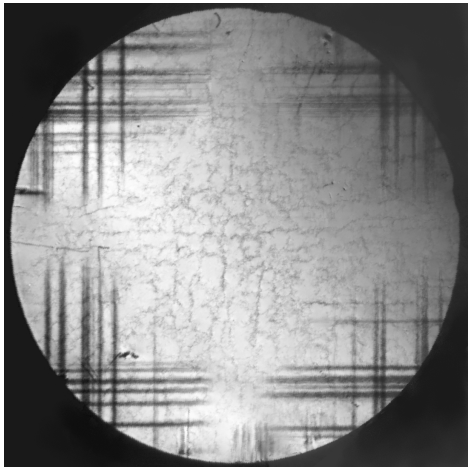


When the slip plane is perpendicular to the applied stress *s*, the angle ? is 90° and no shear stress is resolved.

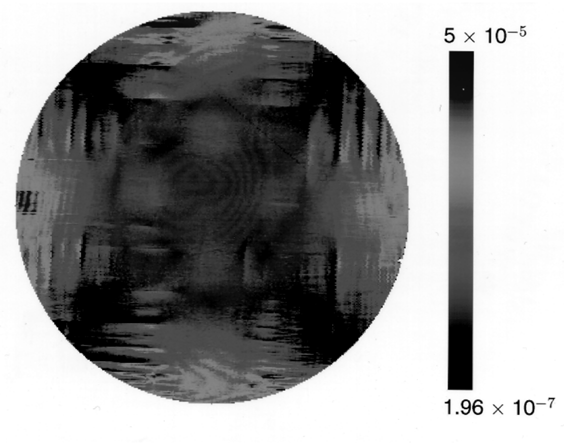
But there will be other slip planes symmetrically equivalent to this one which will have a resolved shear stress on them

P. Möck, J. Appl. Cryst. 34 (2001) 65 - 75

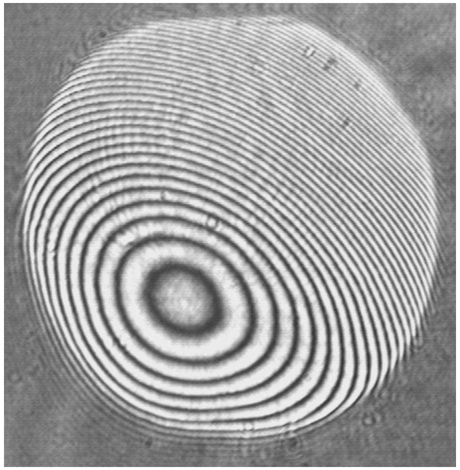
unintentional plastic deformation of GaAs wafers and ingots



X-ray topography at a synchrotron reveals dislocation structure



Scanning infrared polariscopy quantifies shear strains



Visible light interferometry measures surface steps

From a series of X-ray topograms, the dislocation types and their slip systems were derived, tables next page, symmetry and Curie’s symmetry principle reduced experimental effort significantly

From the scanning infrared polariscopy, the levels of strain were derived and converted into stresses that must have existed

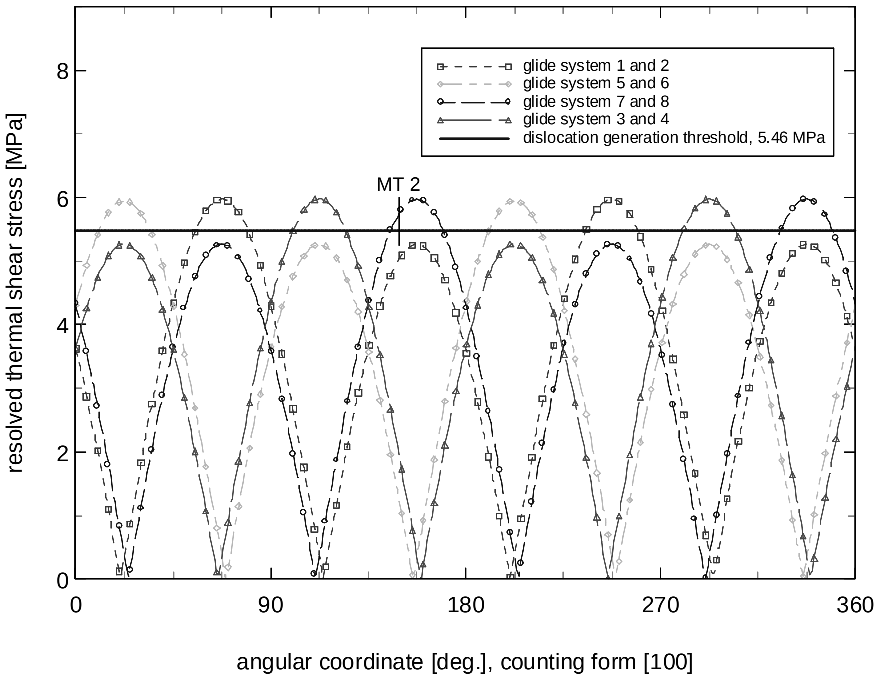
As referred to in the paper	**Line direction***	**Burgers vector, type no. 1**	**Burgers vector, type no. 2**	**"Effective" Burgers vector****
Marker A1	[110]	± ½ [011]	± ½ [10-1]	± ½ [110]
Marker A2	[-1-10]	± ½ [0-1-1]	± ½ [-101]	± ½ [-1-10]
Marker B1	[-110]	± ½ [0-11]	± ½ [10-1]	± ½ [1-10]
Marker B2	[1-10]	± ½ [01-1]	± ½ [-101]	± ½ [-110]
Marker C1	[-1-10]	± ½ [0-11]	± ½ [-10-1]	± ½ [-1-10]
Marker C2	[110]	± ½ [01-1]	± ½ [101]	± ½ [110]
Marker D1	[1-10]	± ½ [011]	± ½ [-10-1]	± ½ [-110]
Marker D2	[-110]	± ½ [0-1-1]	± ½ [101]	± ½ [1-10]

As referred to in the paper	Glide plane	Type of plane according to Gatos & Lavine (1960)	Peripheral areas of origin
Markers A1 and A2	(1-11)	B	[0-10], [100]
Markers B1 and B2	(111)	A	[100], [010]
Markers C1 and C2	(-111)	B	[010], [-100]
Markers D1 and D2	(-1-11)	A	[-100], [0-10]

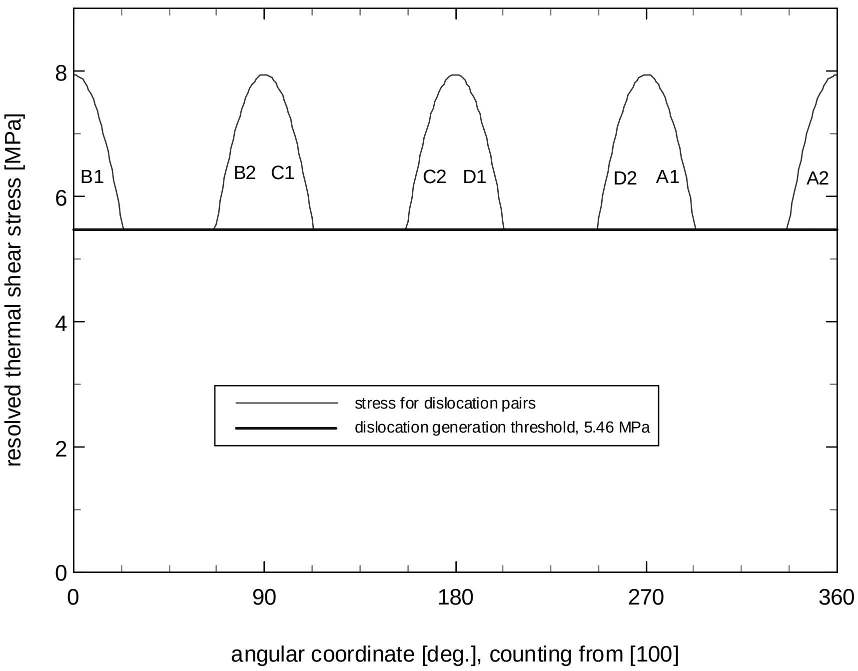
Schmid's law as applied to calculate resolved shear stresses

The critical resolved shear stress was taken from the literature (derived experimentally for same stress stage and single crystalline GaAs wafer, result is an exact match of theoretical predictions where dislocations should be and experimental observations

isolated dislocations, forming minority type dislocation bundles



dislocation pairs, forming majority type dislocation bundles



Þ ***reconstruction of*** temperature field ***that is likely to have caused observed*** plastic deformation

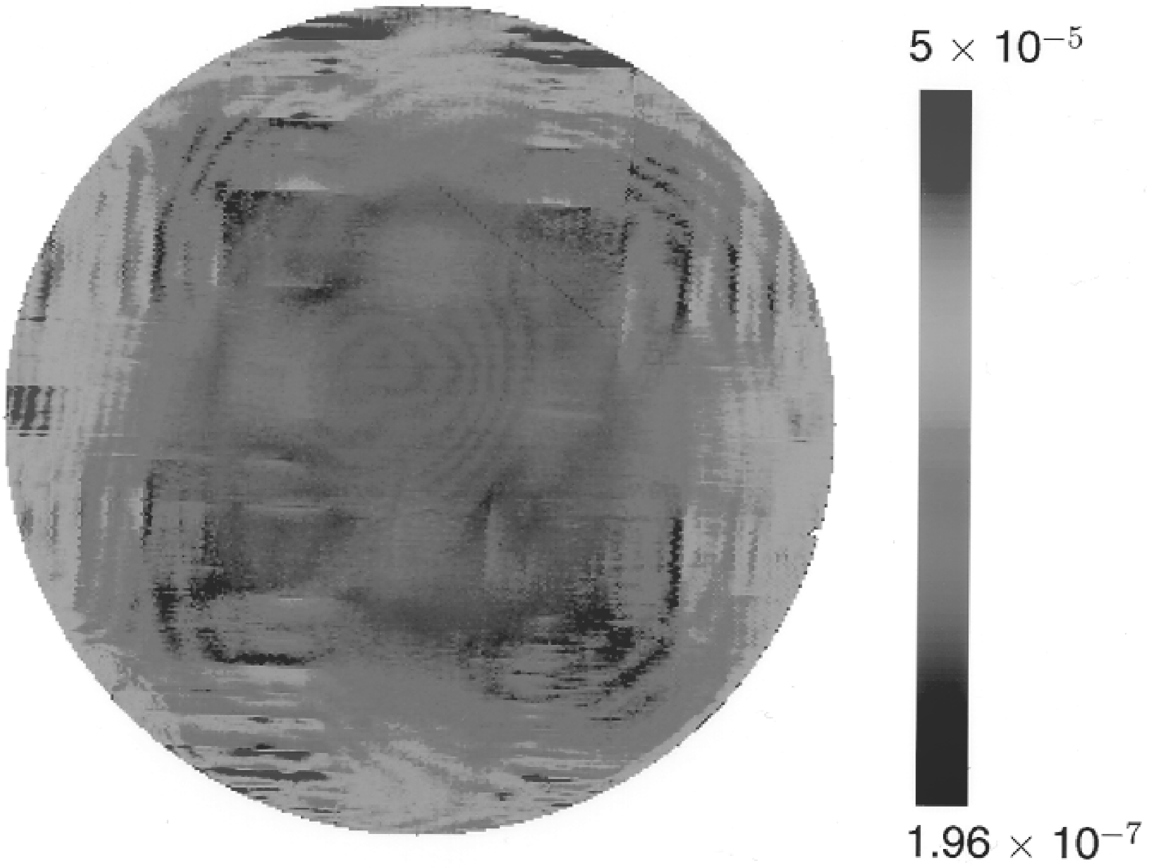
my collaborators at molecular beam epitaxy machine at the Defense Research and Evaluation Agency, Great Malvern, modification to the sample holder of a $ 1 000,000 piece of equipment by, plastic deformation gone for good, P. Möck and G. Smith, Cryst. Res. Technol. 35 (2000) 541-548

Why did I do that? Serendipity

Since I could convince Engineering and Physical Research Council, Great Britain, that this is an unsolved technically relevant problem, I got free access to a very intense X-ray source, travel expenses, accommodation over there, consumables,

all in all not more than £ 15,000 over two years

WORK in pretty slow progress



Pretty similar experimental observations on 3 inch diameter crystal cut from an as grown GaAs crystal, so same or similar deformation mechanism may apply, when proven, radial temperature gradient can be calculated in the same way, modifications to the equipment by made by the engineers

At elevated temperatures (about one half of melting temperature and above) dislocation move pretty fast by diffusion of the individual atoms that make up the dislocation, **(- in a typical metal only 5 out of every 100 million make up a dislocation line -),** so there is no longer an external force needed to move the dislocations – they may be considered to be attracted by the "surface forces" - they move to free surfaces where they disappear (or internal surfaces such as grain boundaries where they may react with other dislocations)

All these interaction result in lower energy structures of the system, the high **annealing** temperature make is possible for the atoms to diffuse, the internal stresses give that diffusion a direction, i.e. towards lower energy structures (note that self-diffusion is considered to be isotropic – all other kinds of diffusion have some driving force which ensures that, although it is a statistical process, more net atomic movement takes place in a certain direction due to the driving force)

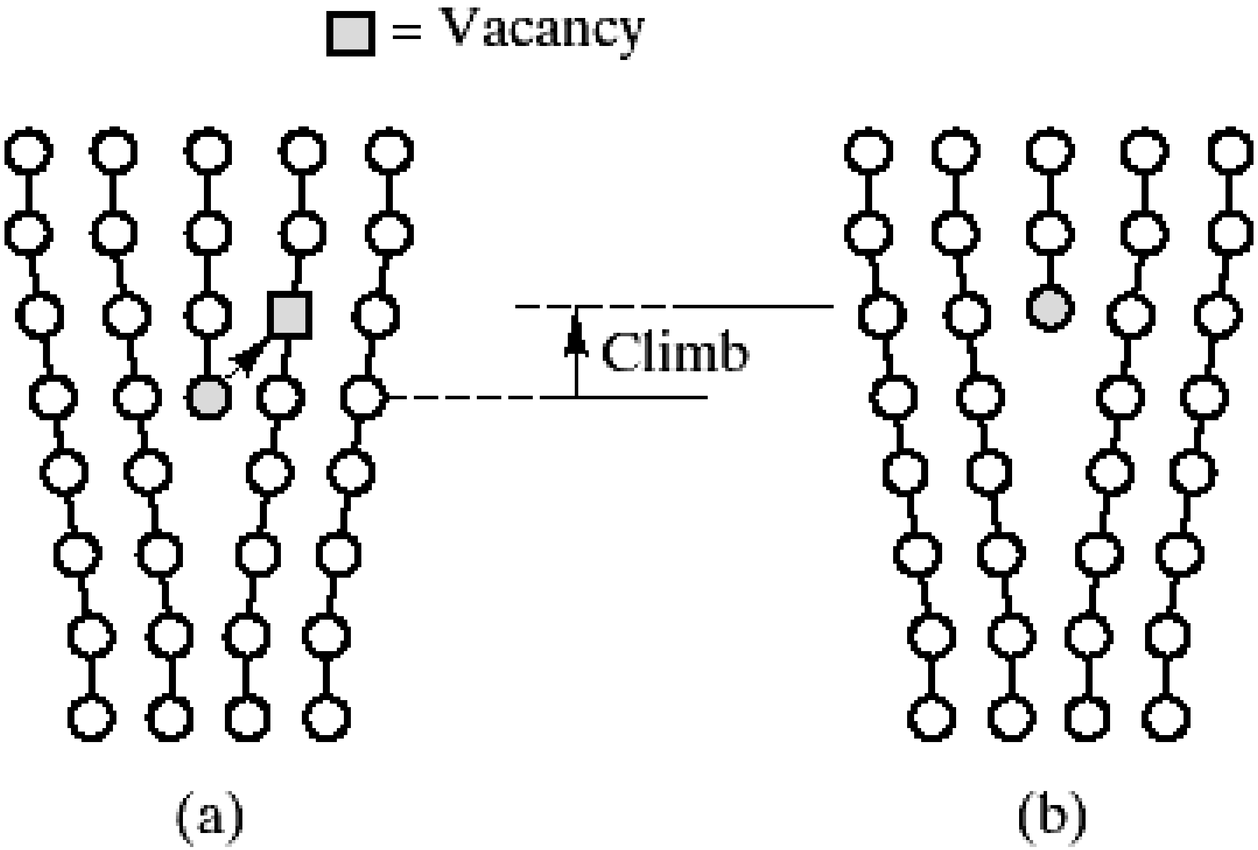


Figure 6-32 ***Mechanism of dislocation climb. Obviously, many adjacent atom movements are required to produce climb of an entire dislocation line.***

Climbing of dislocations happens by diffusion at elevated temperatures

Influence of Crystal Structure and atomic bond strengths

- Critical Resolved Shear Stress – due to bond strengths
- Number of Slip Systems – due to crystallography / 3D structure
- Cross-slip - A change in the slip system of a dislocation, only allowed for certain crystallography, i.e. symmetries

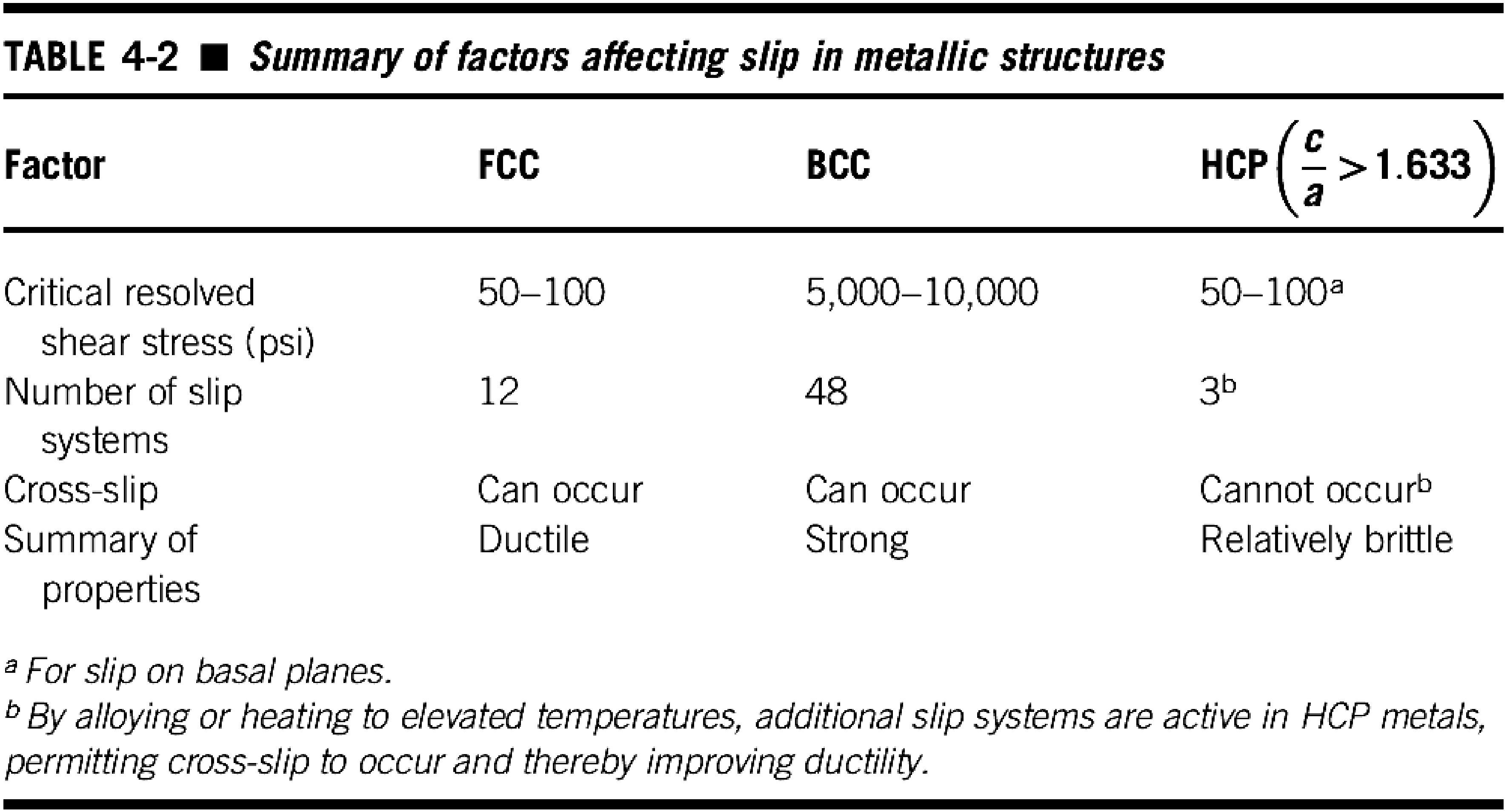


TABLE 4-2 ■ ***Summary of factors affecting slip in metallic structures***

Factor	**FCC**	**BCC**	**HCP** $\left(\frac{c}{a} > 1.633\right)$
Critical resolved shear stress (psi)	50–100	5,000–10,000	50–100[a]
Number of slip systems	12	48	3[b]
Cross-slip	Can occur	Can occur	Cannot occur[b]
Summary of properties	Ductile	Strong	Relatively brittle

[a] *For slip on basal planes.*

[b] *By alloying or heating to elevated temperatures, additional slip systems are active in HCP metals, permitting cross-slip to occur and thereby improving ductility.*

When crystals are deformed, more dislocations are produced, here by a so called Frank-Read source

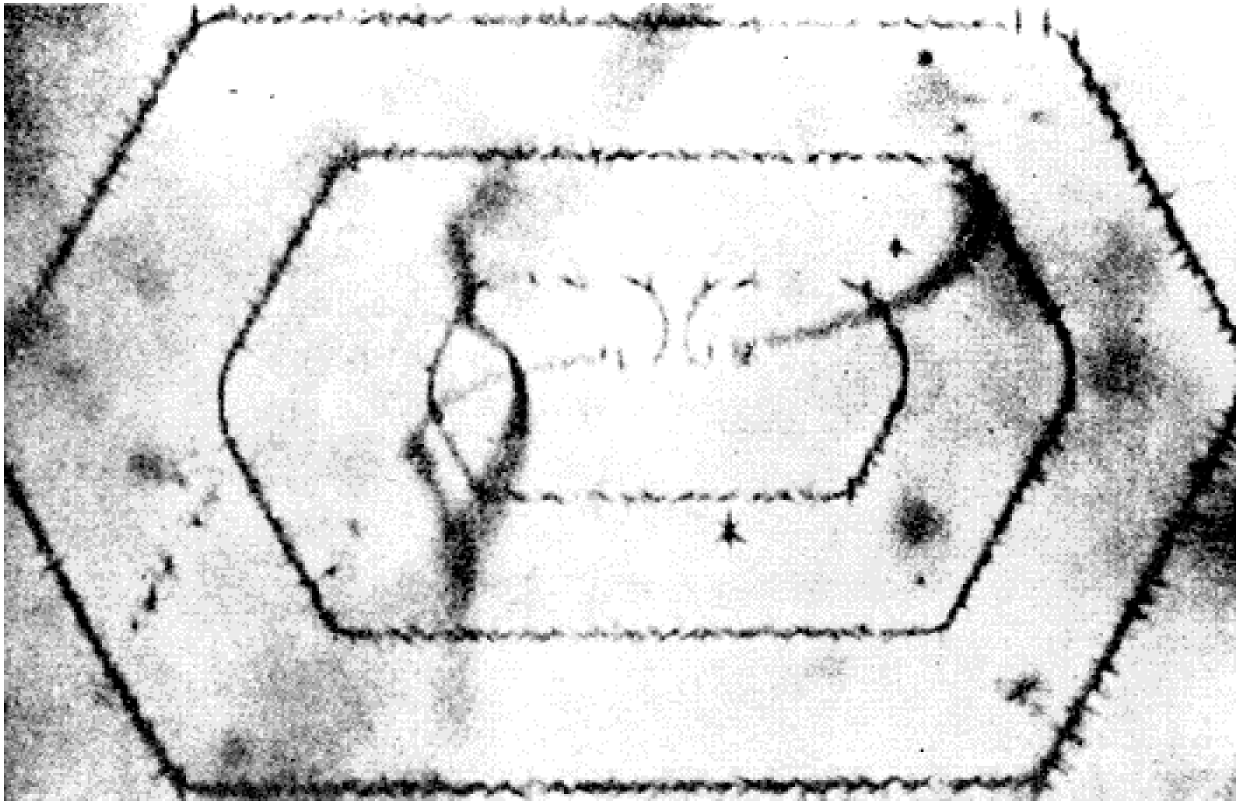


Figure 5.2.20

© The McGraw-Hill Companies, Inc., 1999 Materials In Focus CD ROM

t/a Schaffer: The Science and Design of Engineering Materials, 2/e

Hardness it the resistivity of a material against plastic deformation

As of 1992, there was no exact analytical expression for it, probably there still isn’t one

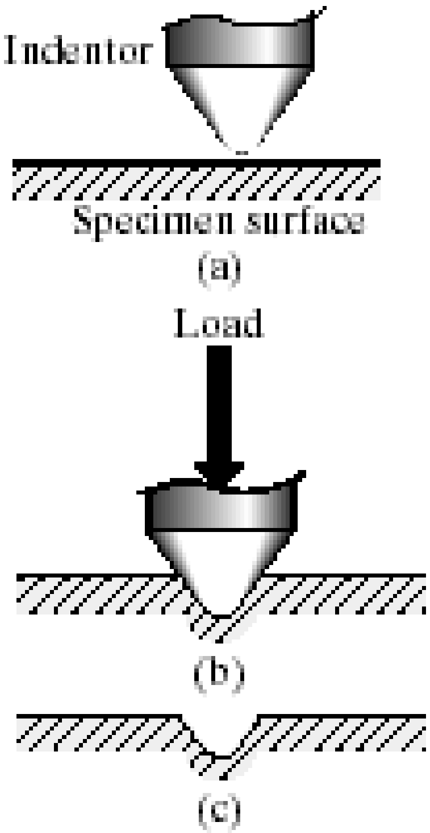
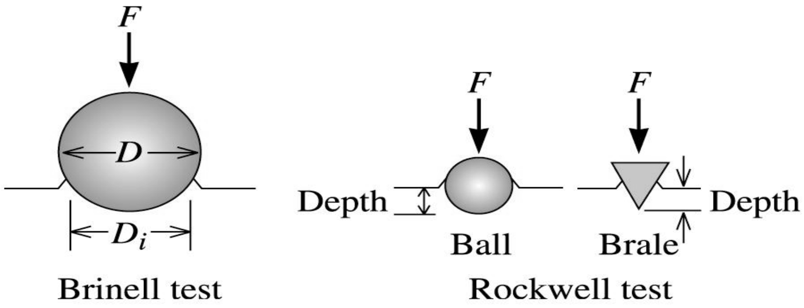


Figure 6-27 *Hardness test. The analysis of indentation geometry is summarized in Table 6.10.*



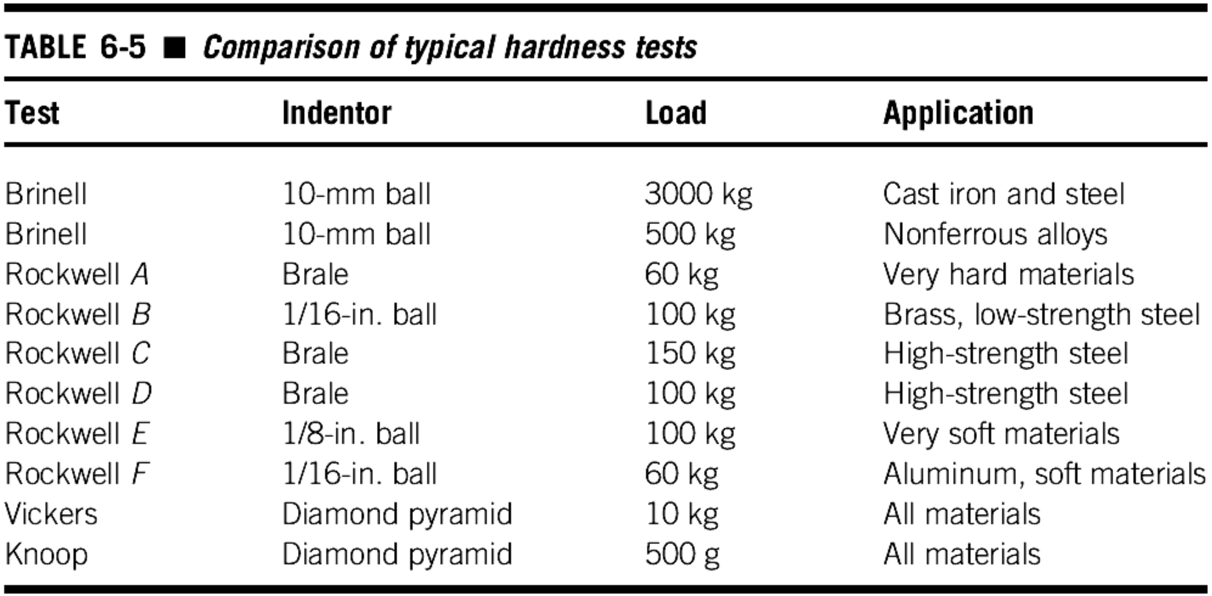


TABLE 6-5 ■ *Comparison of typical hardness tests*

Test	Indentor	Load	Application
Brinell	10-mm ball	3000 kg	Cast iron and steel
Brinell	10-mm ball	500 kg	Nonferrous alloys
Rockwell *A*	Brale	60 kg	Very hard materials
Rockwell *B*	1/16-in. ball	100 kg	Brass, low-strength steel
Rockwell *C*	Brale	150 kg	High-strength steel
Rockwell *D*	Brale	100 kg	High-strength steel
Rockwell *E*	1/8-in. ball	100 kg	Very soft materials
Rockwell *F*	1/16-in. ball	60 kg	Aluminum, soft materials
Vickers	Diamond pyramid	10 kg	All materials
Knoop	Diamond pyramid	500 g	All materials

Mineralogical scale, Mohs hardness, is also used, the harder mineral scratches the softer mineral, deforms it plastically

Plane (area) Defects

- Plane (area) defects - Imperfections, such as grain boundaries, that form a two-dimensional plane within the crystal. The outer surface is the larges of these kinds of defects, we can also speak of these defects as inner surface defects when inside the crystalline materials
- Hall-Petch equation - The relationship between yield strength and grain size in a metallic material—that is,

$$\sigma_y = \sigma_0 + Kd^{-1/2}$$

- Small angle grain boundary - An array of dislocations causing a small misorientation of the crystal across the surface of the imperfection.
- Large angle grain boundaries can have special crystallographic orientations, coincidence site lattices

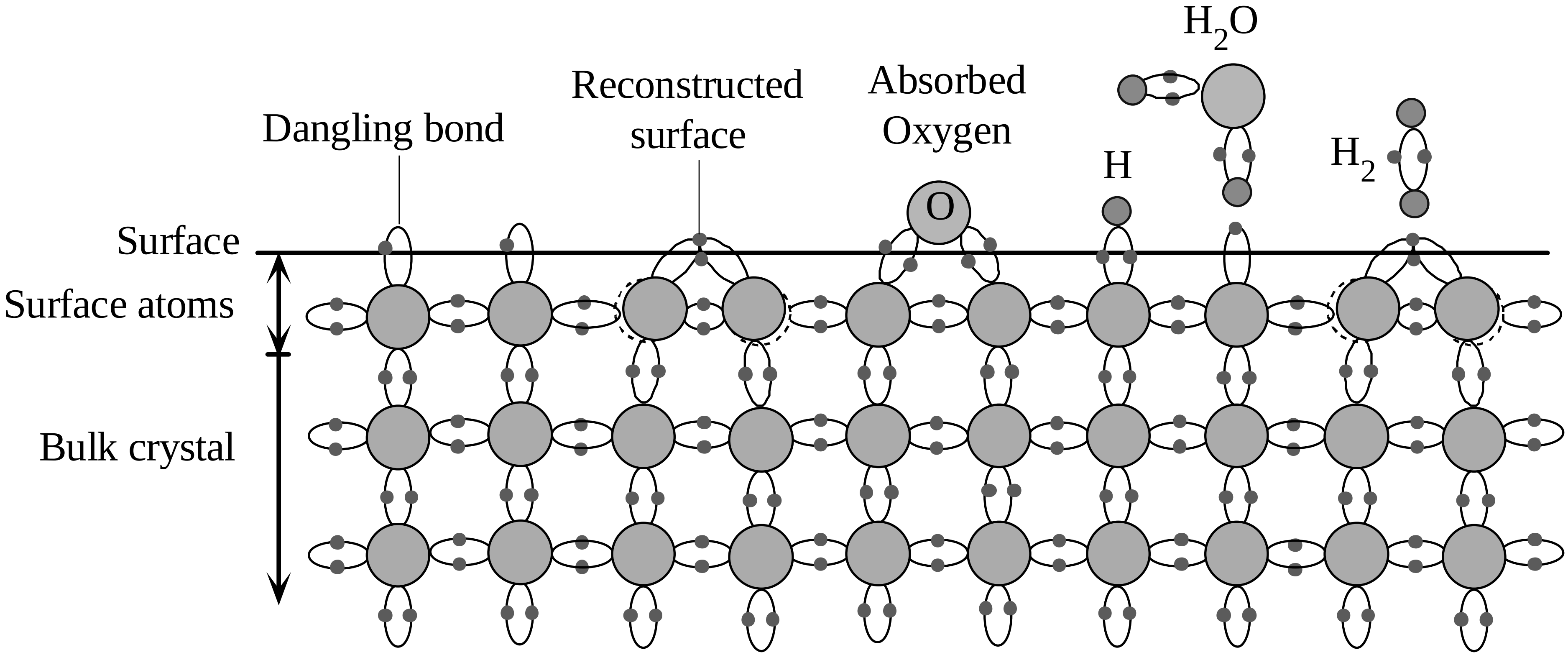


Fig. 1.52: At the surface of a hypothetical two dimensional crystal, the atoms cannot fulfill their bonding requirements and therefore have broken, or dangling, bonds. Some of the surface atoms bond with each other; the surface becomes reconstructed. The surface can have physisorbed and chemisorbed atoms.

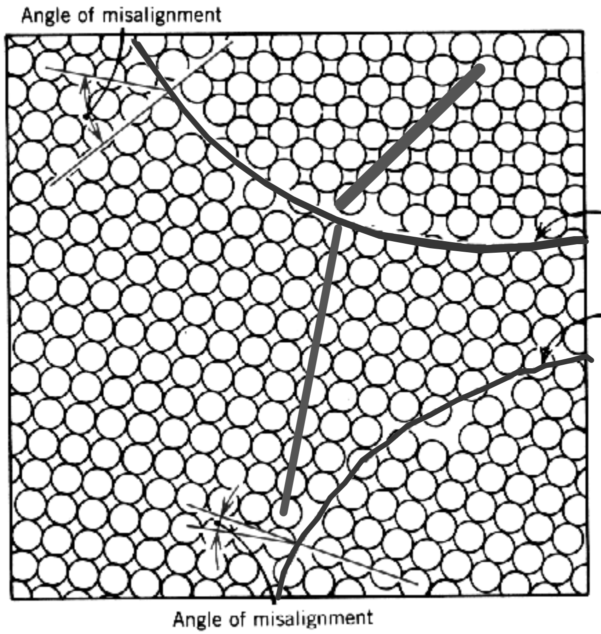
The lattice constant at the surface changes as well.

area defects: grain boundaries

Grain boundaries:

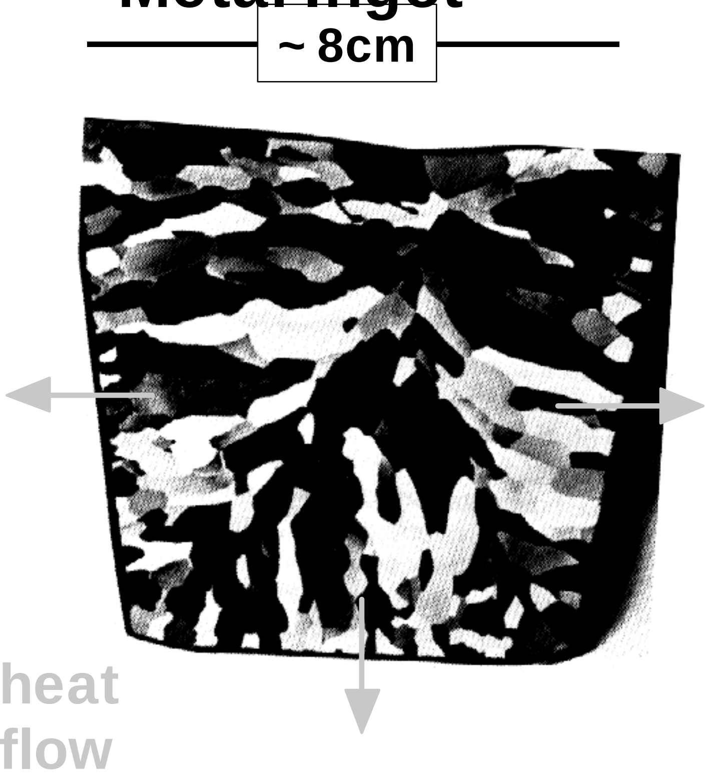
- **are boundaries between crystallites.**
- **are produced by the solidification process, for example.**
- **have a large change in crystal orientation across them.**
- **impede dislocation motion.**

Schematic



grain boundaries

Metal Ingot



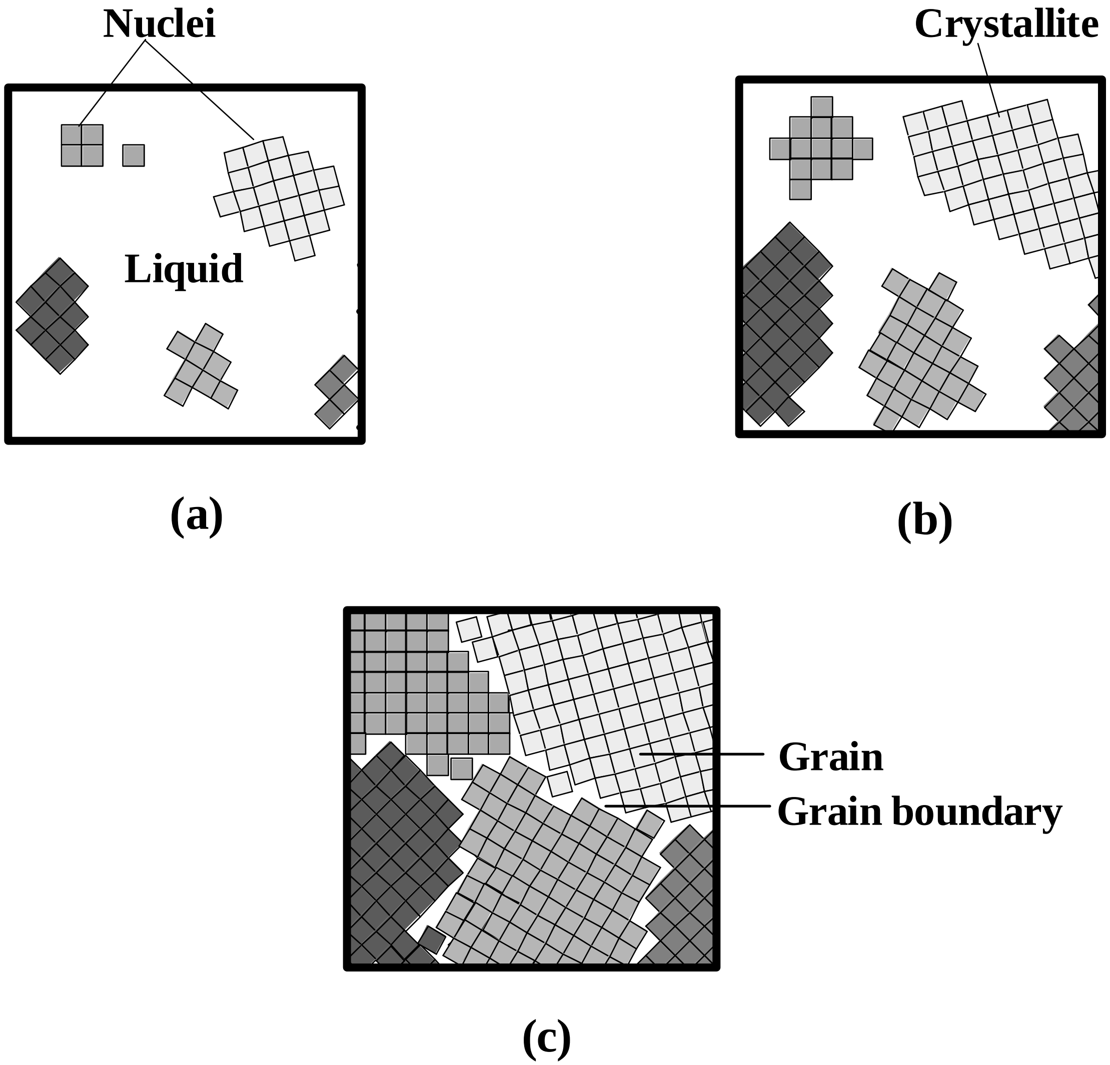
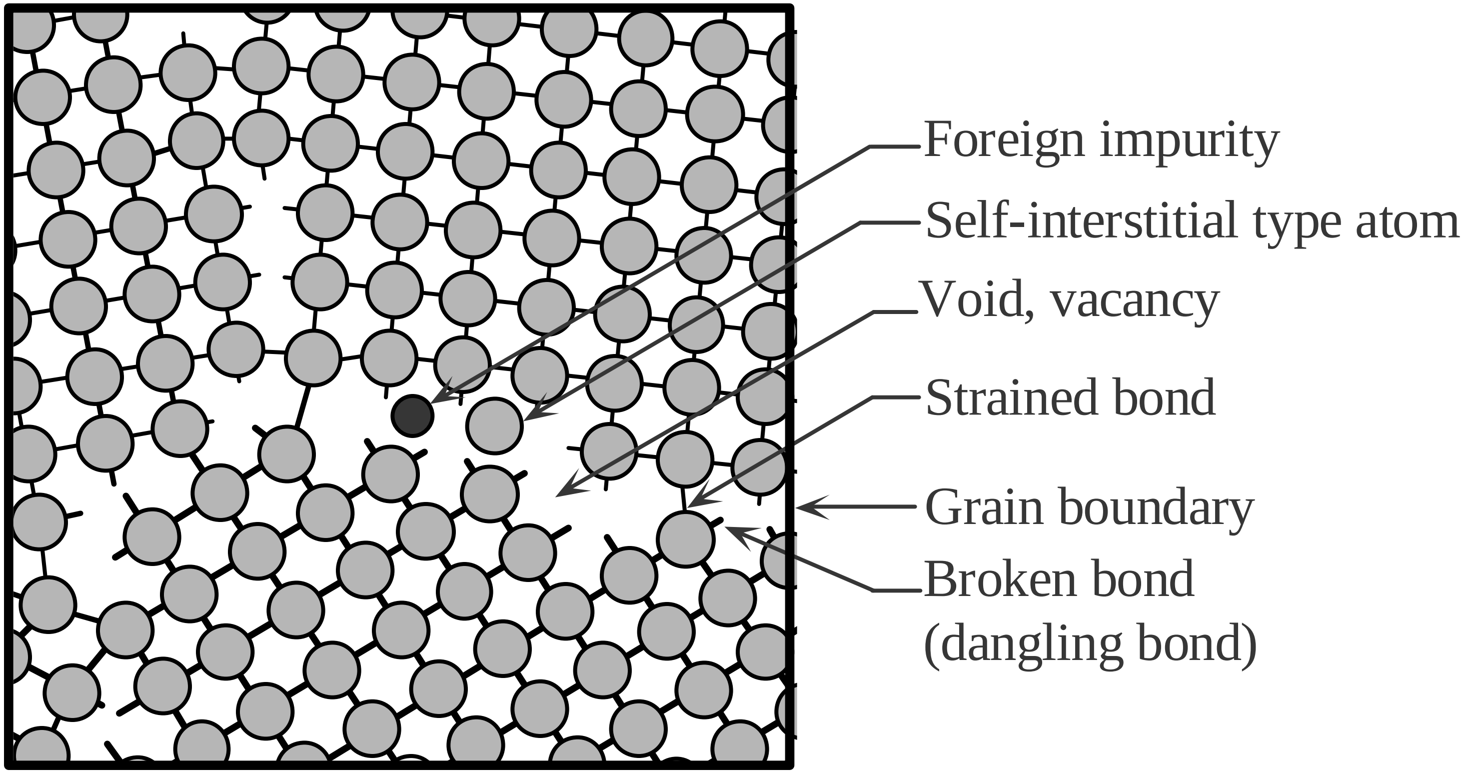


Fig. 1.50: Solidification of a polycrystalline solid from the melt. (a) Nucleation. (b) Growth. (c) The solidified polycrystalline solid. For simplicity, cubes represent atoms.

But that’s not the only process, cold rolling does produce grain boundaries as well, as they have excess energy, grain boundary energy, annealing allows re-growth of the grains, reducing total grain boundary area in the material



Foreign impurity

Self-interstitial type atom

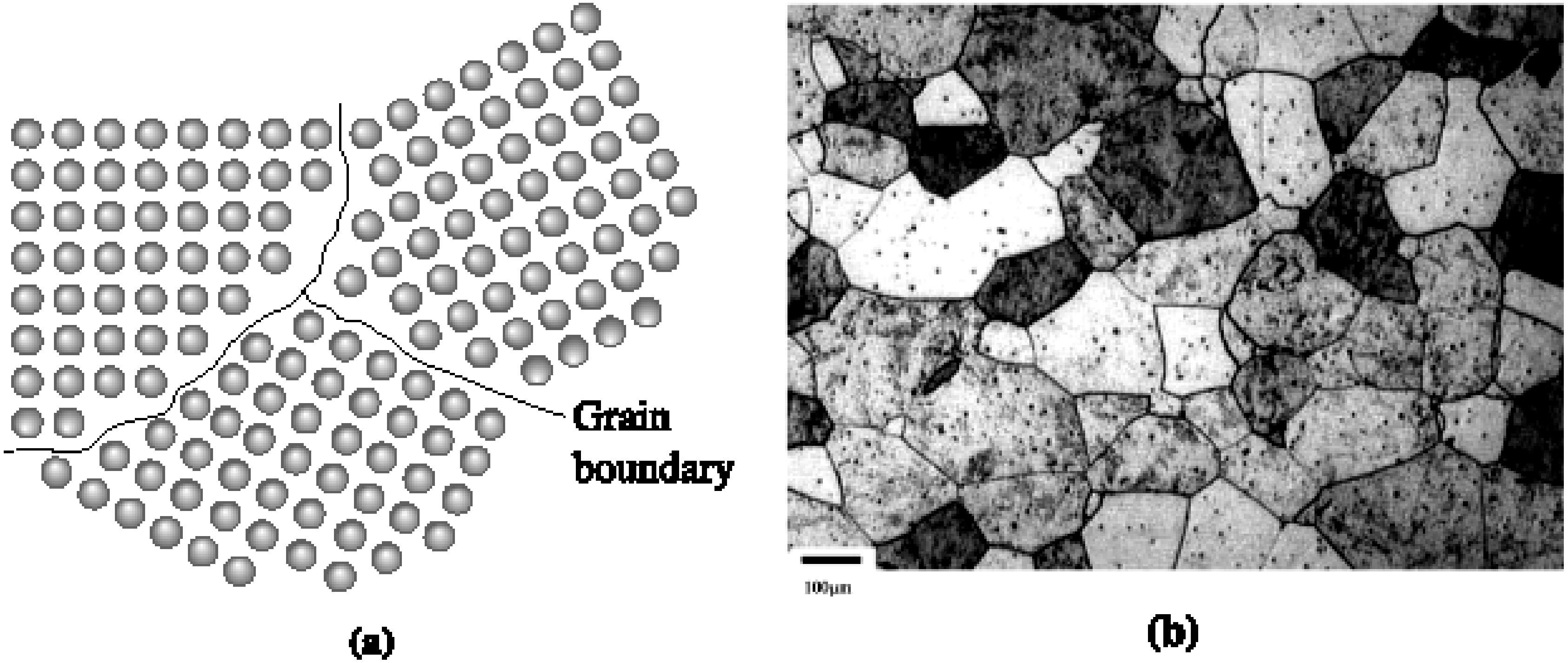
Void, vacancy

Strained bond

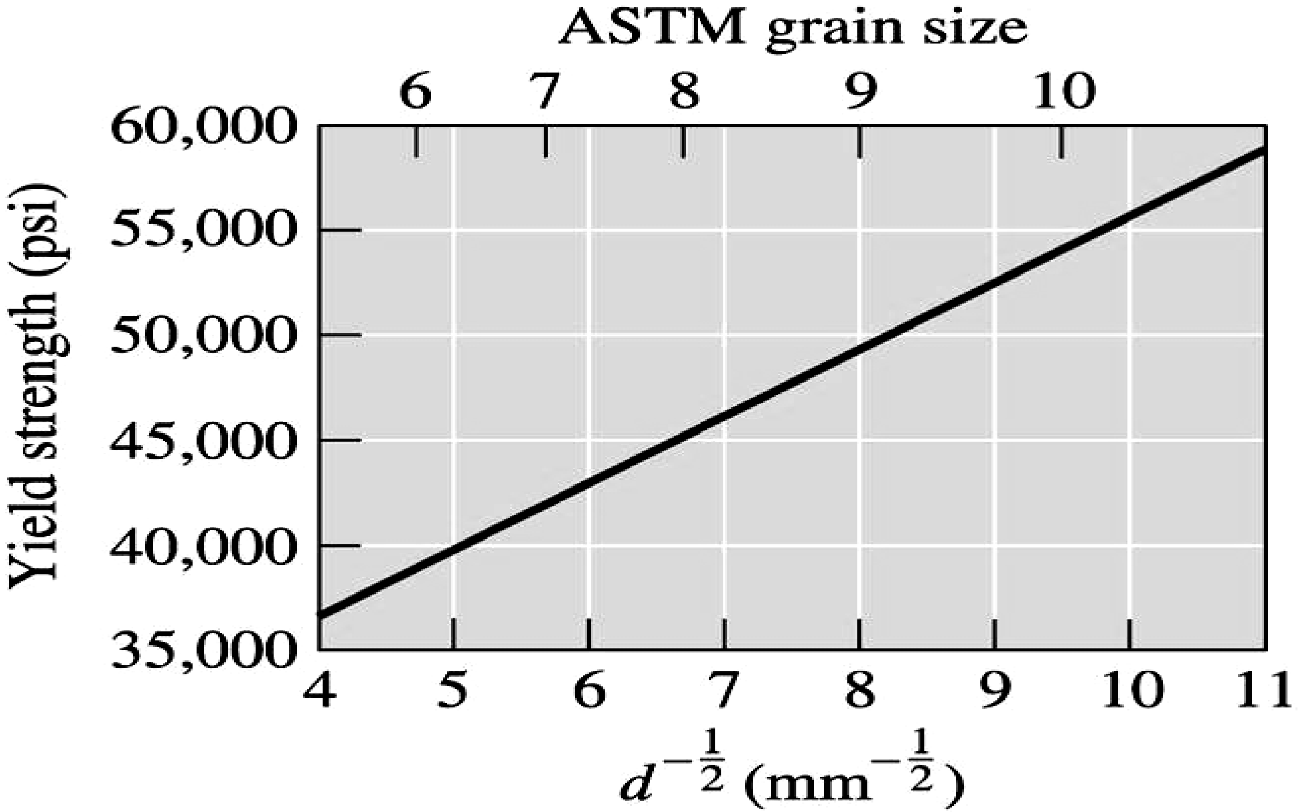
Grain boundary

Broken bond
(dangling bond)

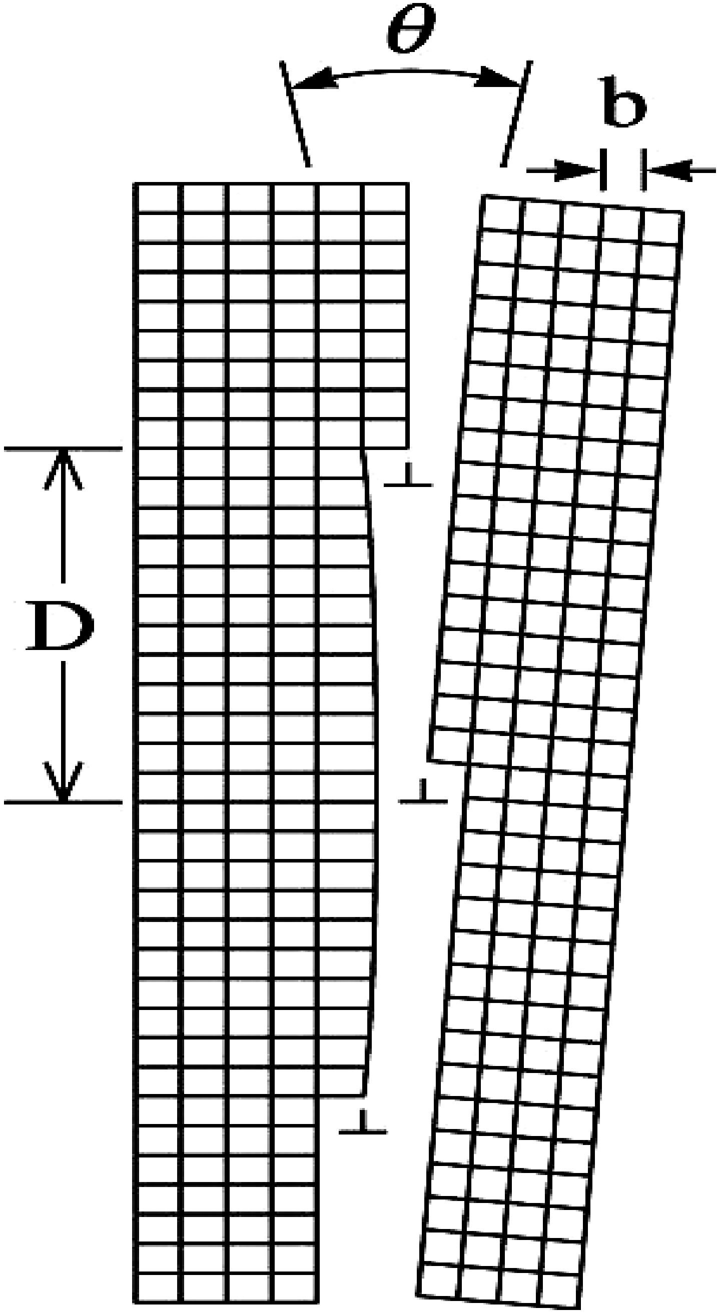
Fig. 1.51: The grain boundaries have broken bonds, voids, vacancies, strained bonds and "interstitial" type atoms. The structure of the grain boundary is disordered and the atoms in the grain boundaries have higher energies than those within the grains.



(a) The atoms near the boundaries of the three grains do not have an equilibrium spacing or arrangement. (b) Grains and grain boundaries in a stainless steel sample.



The effect of grain size on the yield strength of steel at room temperature. Just as we discussed for nanostructured materials, the smaller the grain the more grain boundary area, the more dislocation glide is impeded, the stronger the material, it may not be as ductile, however, and fail under too heavy a load in a brittle manner



The small angle grain boundary is produced by / can be thought of consisting of an array of dislocations, causing an angular mismatch ? between lattices on either side of the boundary.

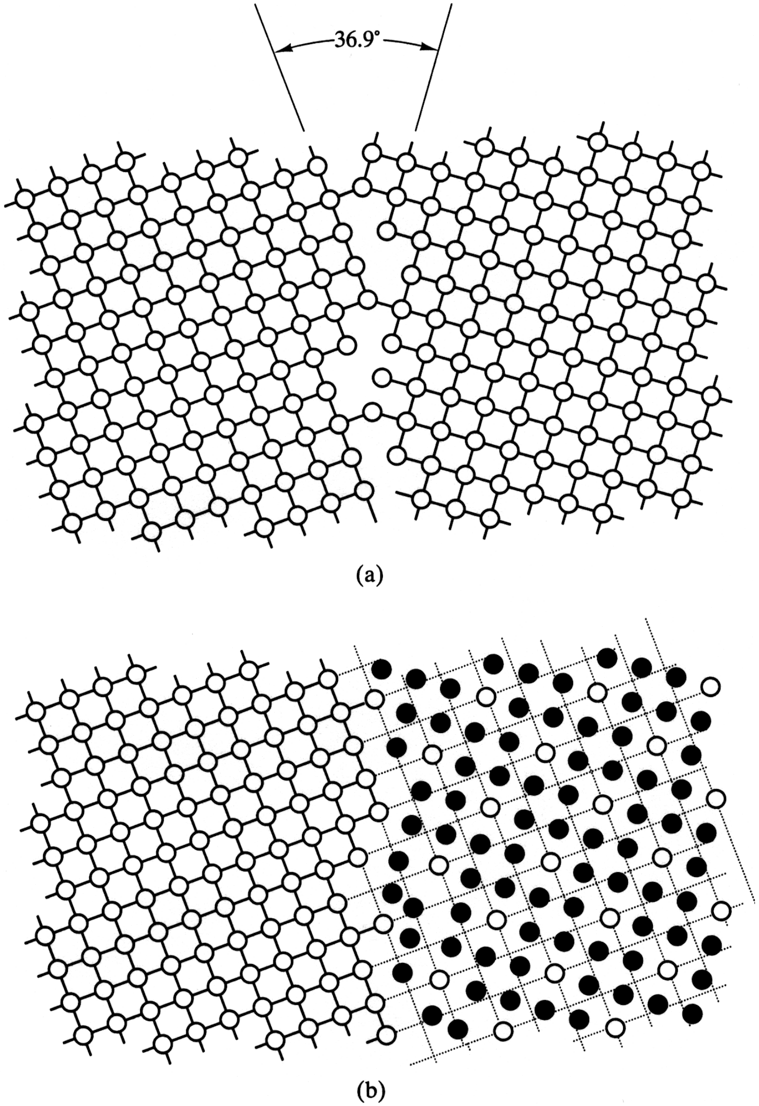
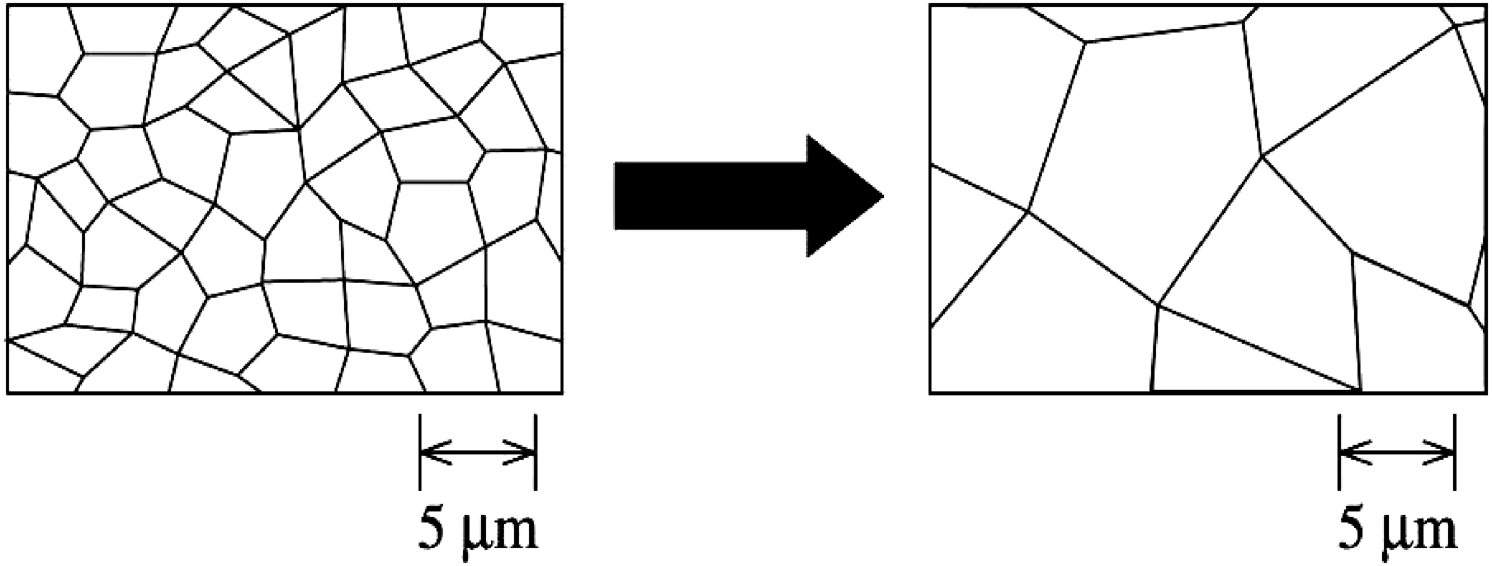


Figure 4-20 *(a) A high-angle ($\theta = 36.9°$) grain boundary between two square lattice grains can be represented by a coincidence site lattice, as shown in (b). As one in five of the atoms in the grain on the right is coincident with the lattice of the grain on the left, the boundary is said to have $\Sigma^{-1} = 1/5$, or $\Sigma = 5$.*

Large angle grain boundaries have frequently a special orientation relationships that are due to low energy structures,

its called coincidence site lattices as a certain fraction of the atom sites are common in the two crystals that interface at the grain boundary

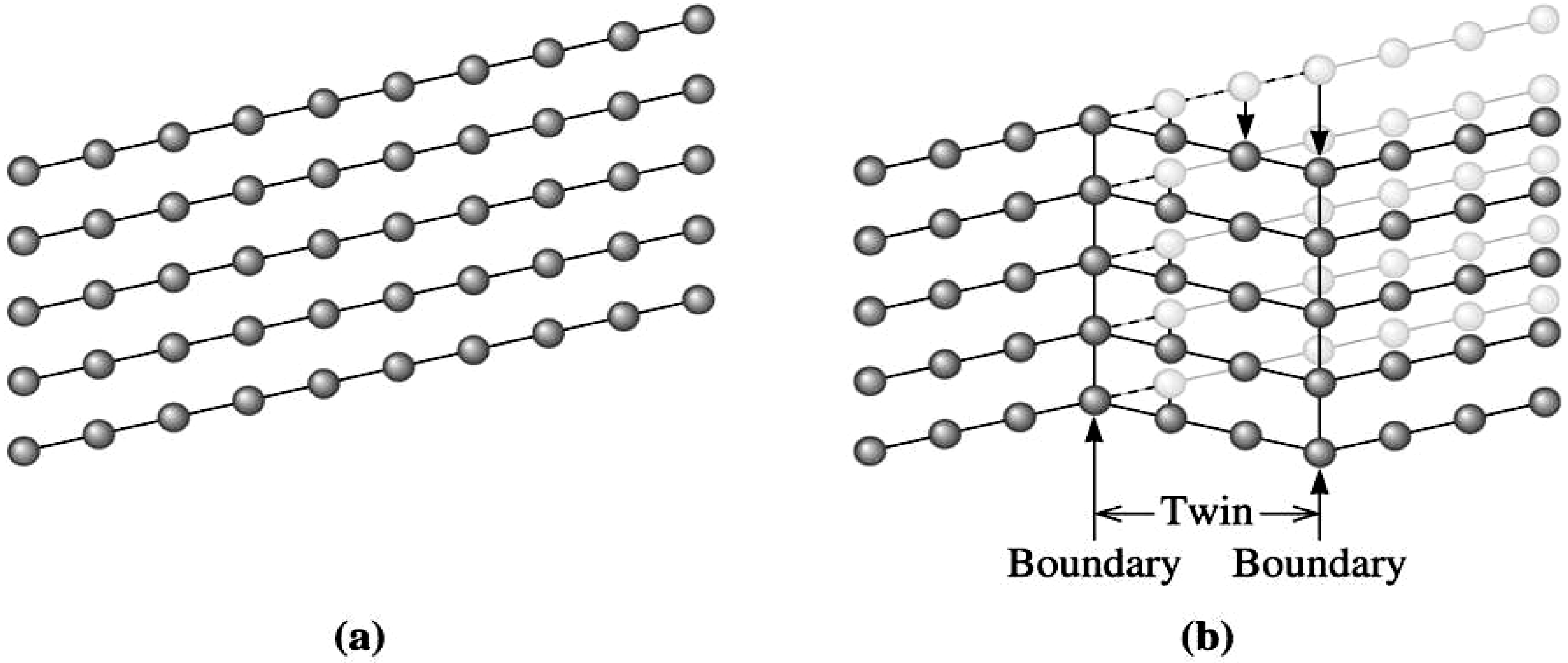


(a) Initial microstructure **(b)** Microstructure after grain growth

Grain growth occurs as atoms diffuse across the grain boundary from one grain to another, low energy grain boundaries, i.e. coincidence site lattice boundaries are also formed by diffusion due to heat treatments

As diffusion depends critical (exponentially) on temperature, this grain grow is fast at temperatures around 0.5 melting temperature – annealing procedure

Twins: two crystals together, the symmetry operation needed to go from one crystal to the other is in excess of the symmetry operation of these crystals



Application of a stress to the perfect crystal (a) may cause a special displacement of the atoms, (b) causing the formation of a twin and corresponding plastic deformation. Shape memory alloys work on a twinning-untwinning mechanism that can be controlled by changes in temperature

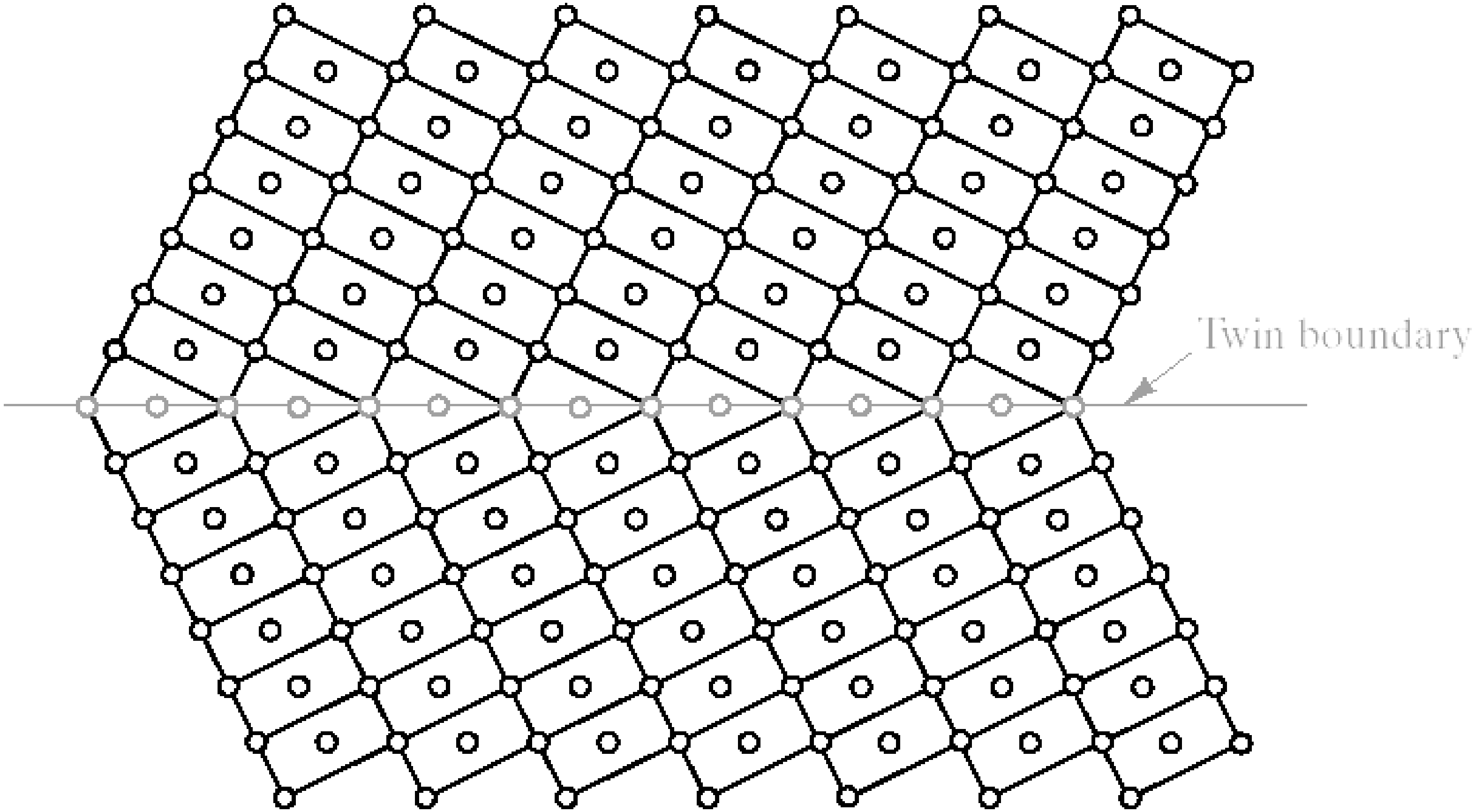
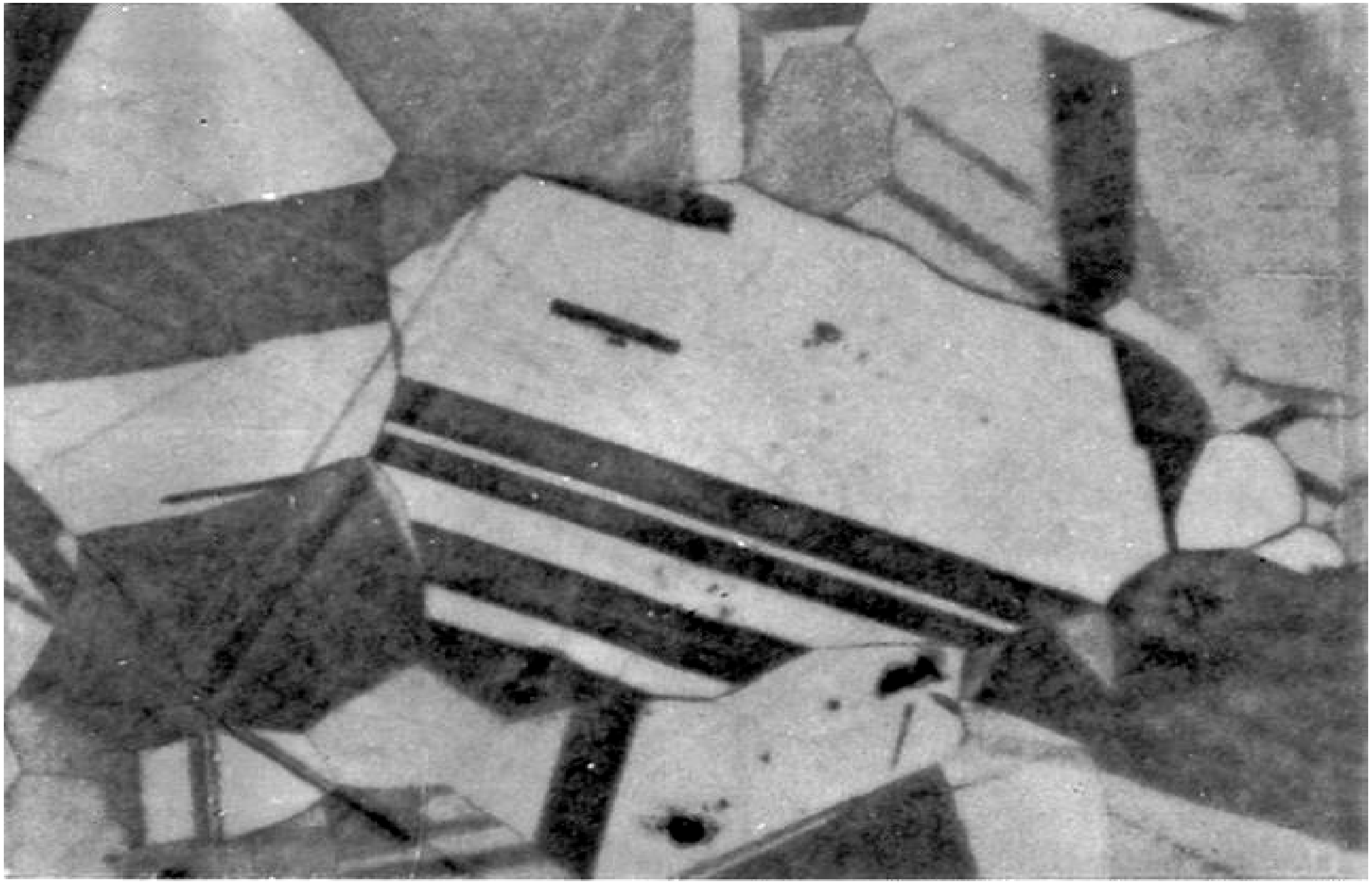


Figure 4-15 *A twin boundary separates two crystalline regions that are, structurally, mirror images of each other.*



(c)

(An optical micrograph of twins within a grain of brass (x 250).

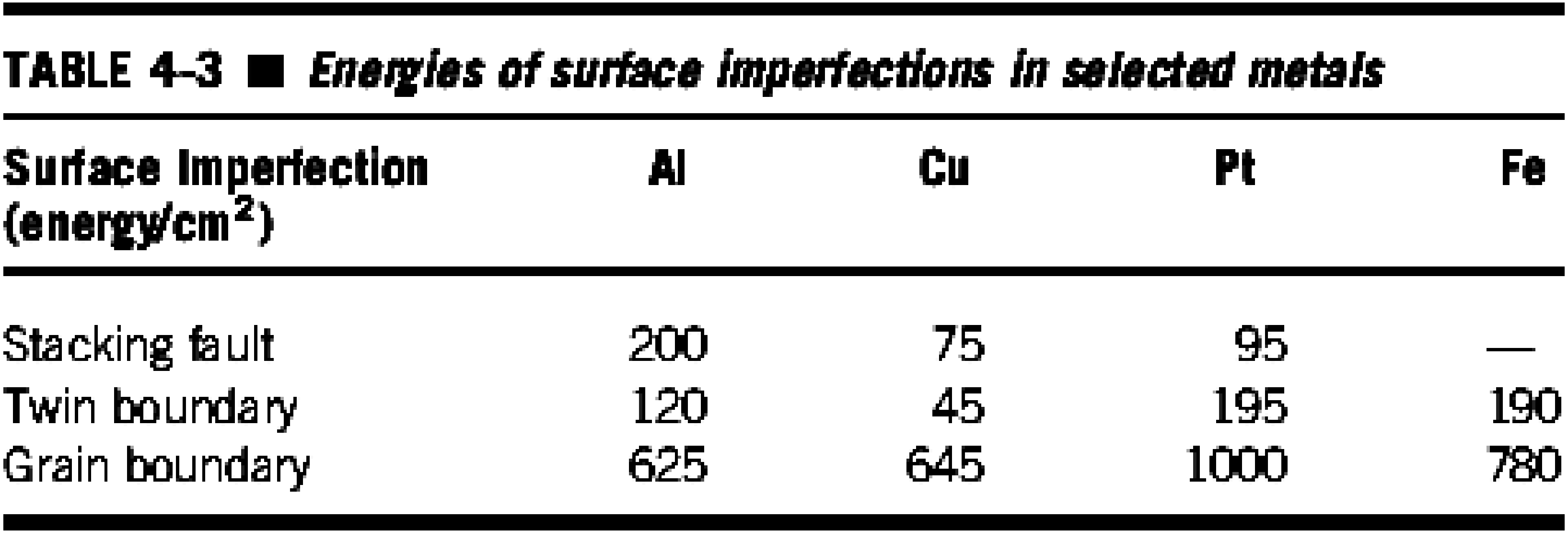


TABLE 4-3 ■ ***Energies of surface imperfections in selected metals***

Surface Imperfection (energy/cm^2)	Al	Cu	Pt	Fe
Stacking fault	200	75	95	—
Twin boundary	120	45	195	190
Grain boundary	625	645	1000	780

Note the low energy of twins, so they are very common area defects

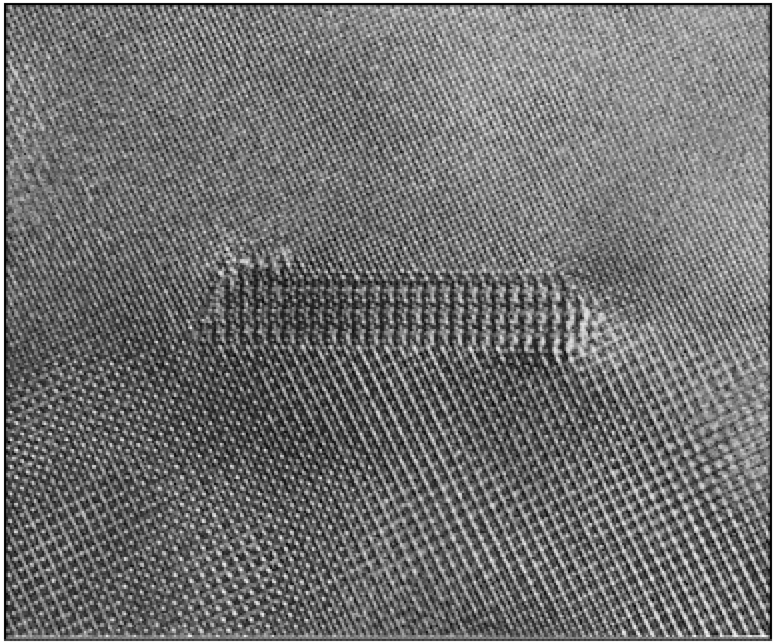
Volume defects

All defects that are 3D in their nature,

here a precipitate in TEM

in first lecture we had also an STEM image of a void in Si that was at its interface with the Si partially lined by Sn,

there may also be cracks, pores, ...



(c)

Figure 8.2.8c
© The McGraw-Hill Companies, Inc., 1999 Materials in Focus CD ROM
t/a Schaffer: The Science and Design of Engineering Materials, 2/e

Precipitates of alien phases frequently sit at grain boundaries – as in the image above - these are places of reduced formation energy for the precipitate since the crystal structure is severely disturbed there

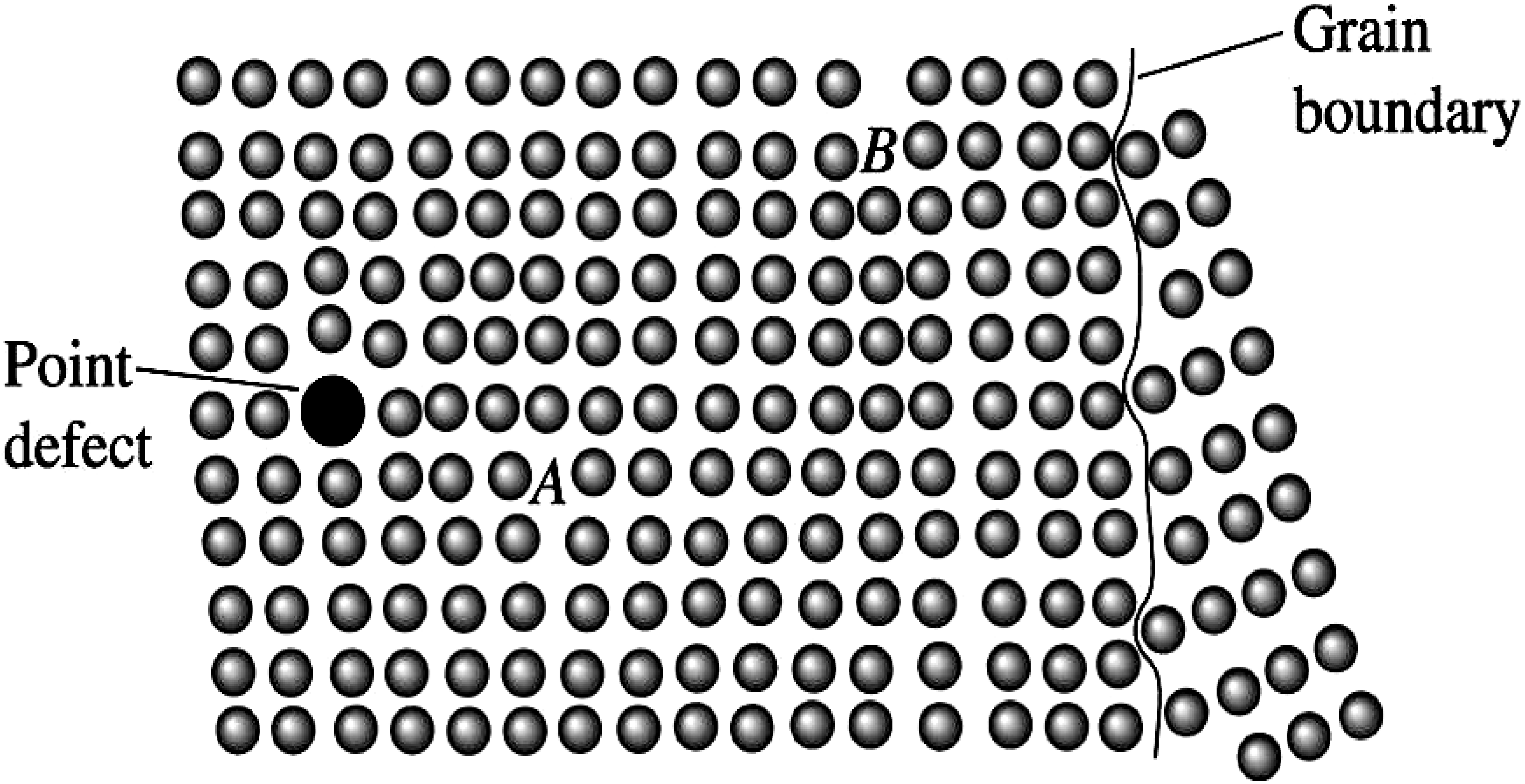
Importance of Defects

- Effect on Mechanical Properties via Control of the Slip Process
- Work Hardening, just like forging of metals, having produced lots of dislocations, it is difficult for these dislocations to move and mediate plastic deformation

Solid-Solution Strengthening/hardening – the basis idea of alloying, creating volume defects

Grain-Size Strengthening/hardening as discussed with nanostructured materials

- Significant Effects on Electric, Dielectric, Optical, and Magnetic Properties



If the dislocation at point *A* moves to the left, it is blocked by the point defect. If the dislocation moves to the right, it interacts with the disturbed lattice near the second dislocation at point *B*. If the dislocation moves farther to the right, it is blocked by a grain boundary.

Catastrophic failure of the so called "freedom ships"

USS Schenectady

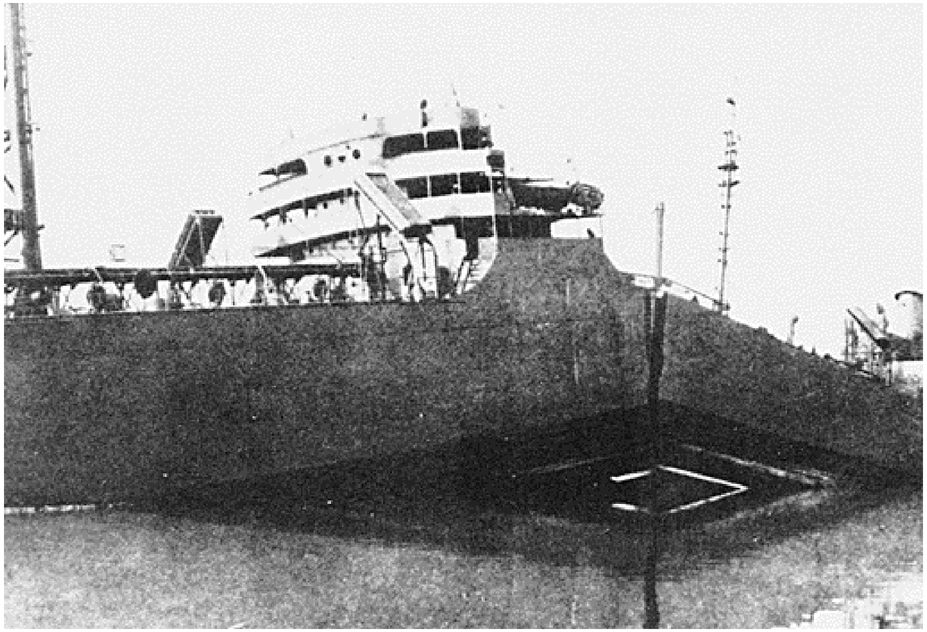


Figure 9.3.1
© The McGraw-Hill Companies, Inc., 1999 Materials in Focus CD ROM
t/a Schaffer: The Science and Design of Engineering Materials, 2/e

Brittle fracture may occur if a material can't react to stresses by dislocation glide

The hull of these ships was welded, poor quality steel was used towards end of WWII, micro-cracks developed and grew slowly into larger cracks, when they reached the critical size, the final crack proceeded extremely rapidly – now smaller parts of the ship are riveted together and better steels are used

Also brittle fracture of Boeing 737

Chapter 15 Opener Art
© The McGraw-Hill Companies, Inc., 1999 Materials in Focus CD ROM
t/a Schaffer: The Science and Design of Engineering Materials, 2/e

SUMMARY

- **Point, Line, Area, Volume 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.)**

Point defect such as same atom interstitials and vacancies cannot be avoided, are always there in an amount that depends on the temperature

Single Si crystals are free of dislocations, stacking faults, twins, and precipitates – a marvelous feat of engineering