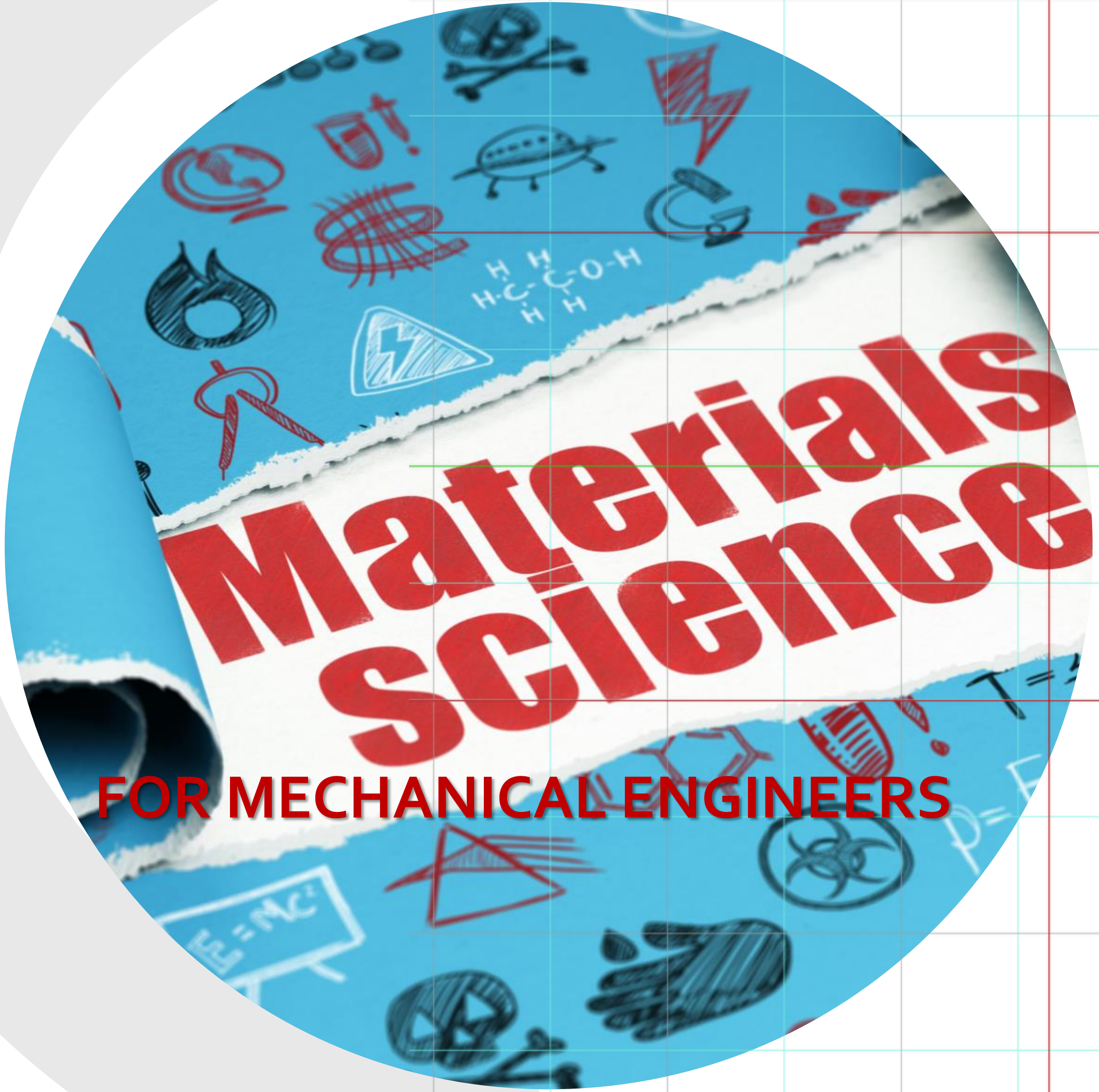


FOR MECHANICAL ENGINEERS

Imperfections in Solids

SPRING 2022-2023

INTRODUCTION

Learning Objectives

- Describe both vacancy and self-interstitial crystalline defects.
- Calculate the equilibrium number of vacancies in a material at some specified temperature, given the relevant constants.
- Name the two types of solid solutions and provide a brief written definition and/or schematic sketch of each.
- Given the masses and atomic weights of two or more elements in a metal alloy, calculate the weight percent and atom percent for each element.
- For each of edge, screw, and mixed dislocations:
    - (a) describe and make a drawing of the dislocation,
    - (b) note the location of the dislocation line, and
    - (c) indicate the direction along which the dislocation line extends.
- Describe the atomic structure within the vicinity of
    - (a) a grain boundary and
    - (b) a twin boundary.

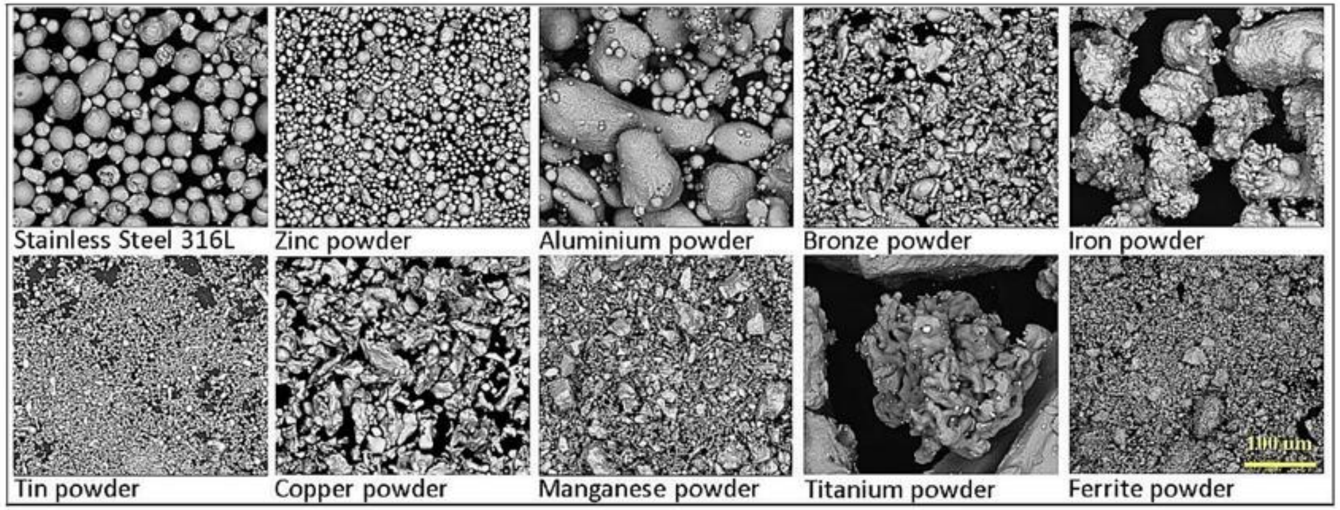
INTRODUCTION

The properties of some materials are profoundly influenced by the presence of imperfections.

Consequently, it is important to have a knowledge about the types of imperfections that exist and the roles they play in affecting the behaviour of materials.

For example, the mechanical properties of pure metals experience significant alterations when the metals are alloyed (i.e., when impurity atoms are added)—for example, brass (70% copper–30% zinc) is much harder and stronger than pure copper.

Also, integrated-circuit microelectronic devices found in our computers, calculators, and home appliances function because of highly controlled concentrations of specific impurities that are incorporated into small, localized regions of semiconducting materials.



INTRODUCTION

Thus far it has been tacitly assumed that perfect order exists throughout crystalline materials on an atomic scale. However, such an idealized solid does not exist; all contain large numbers of various defects or **imperfections.**

As a matter of fact, many of the properties of materials are profoundly sensitive to deviations from crystalline perfection; the influence is not always adverse, and often specific characteristics are deliberately fashioned by the introduction of controlled amounts or numbers of particular defects.

A *crystalline defect* refers to a lattice irregularity having one or more of its dimensions on the order of an atomic diameter. Classification of crystalline imperfections is frequently made according to the geometry or dimensionality of the defect.

Several different imperfections will addressed, including **point defects** (those associated with one or two atomic positions); linear (or one-dimensional) defects; and interfacial defects, or boundaries, which are two-dimensional.

Impurities in solids are also discussed, because impurity atoms may exist as point defects.

Finally, techniques for the microscopic examination of defects and the structure of materials are briefly described.

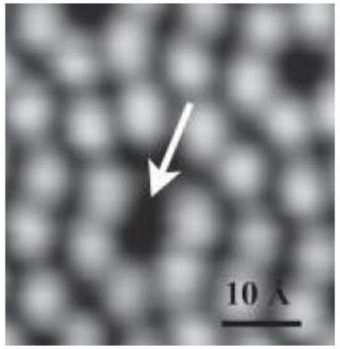
POINT DEFECTS

VACANCIES AND SELF-INTERSTITIALS

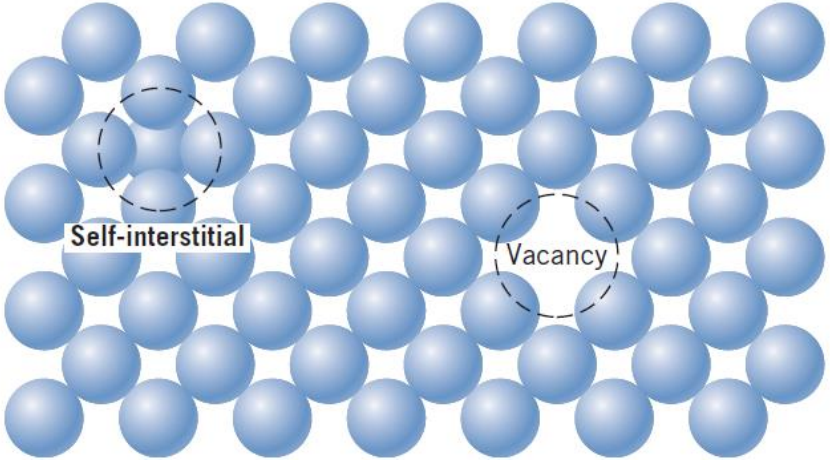
The simplest of the point defects is a **vacancy,** or vacant lattice site, one normally occupied but from which an atom is missing.

All crystalline solids contain vacancies, and, in fact, it is not possible to create such a material that is free of these defects.

The necessity of the existence of vacancies is explained using principles of thermodynamics; in essence, the presence of vacancies increases the entropy (i.e., the randomness) of the crystal.



Scanning probe micrograph that shows a vacancy on a (111)-type surface plane for silicon. Approximately 7,000,000×. (Micrograph courtesy of D. Huang, Stanford University.)



Two-dimensional representations of a vacancy and a self-interstitial.

POINT DEFECTS

The equilibrium number of vacancies N_v for a given quantity of material (usually per meter cubed) depends on and increases with temperature according to

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

is the total number of atomic sites (most commonly per cubic meter), Q_v is the energy required for the formation of a vacancy (J/mol or eV/atom), T is the absolute temperature in kelvins, and k is the gas or **Boltzmann's constant.**

The value of k is 1.38×10^{-23} J/atom·K, or 8.62×10^{-5} eV/atom·K, depending on the units of Q_v. Thus, the number of vacancies increases exponentially with temperature—that is, as T increases, so also does the term $\exp(-Q_v/kT)$.

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

As ensuing discussions indicate, a number of other material parameters have an exponential dependence on temperature similar to that in the equation.

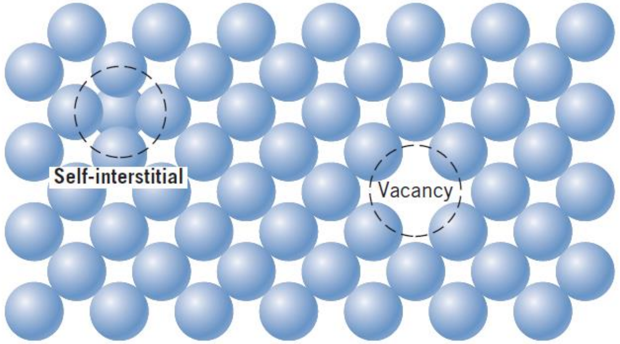
Boltzmann's constant the ratio of the gas constant to Avogadro's constant, equal to 1.381×10^{-23} joules per kelvin in the case where the number of molecules is equal to Avogadro's number.

POINT DEFECTS

A **self-interstitial** is an atom from the crystal that is crowded into an *interstitial site*, a small void space that under ordinary circumstances is not occupied.

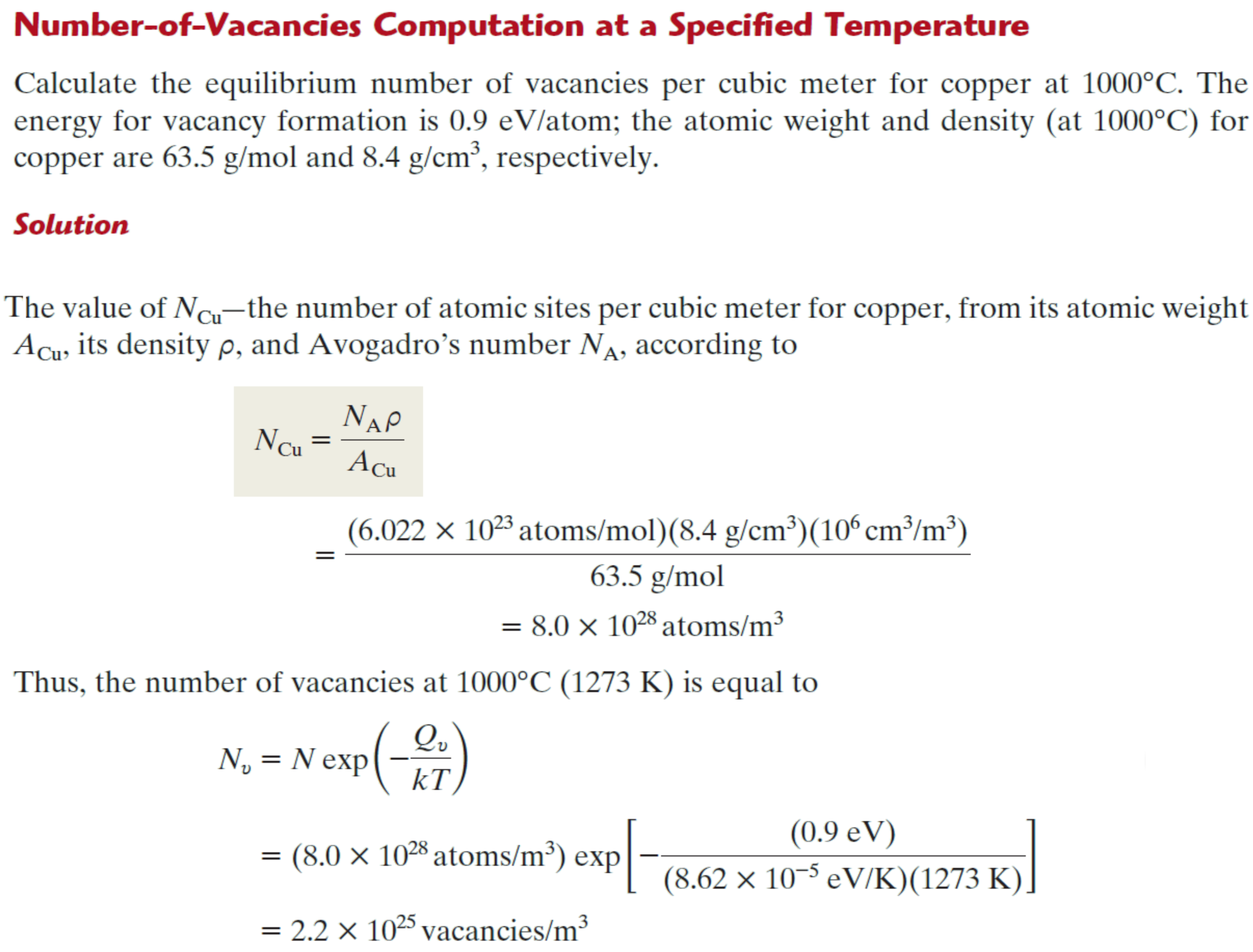
This kind of defect is also represented in the figure. In metals, a self-interstitial introduces relatively large distortions in the surrounding lattice because the atom is substantially larger than the interstitial position in which it is situated.

Consequently, the formation of this defect is not highly probable, and it exists in very small concentrations that are significantly lower than for vacancies.



POINT DEFECTS

EXAMPLE



Number-of-Vacancies Computation at a Specified Temperature

Calculate the equilibrium number of vacancies per cubic meter for copper at 1000°C. The energy for vacancy formation is 0.9 eV/atom; the atomic weight and density (at 1000°C) for copper are 63.5 g/mol and 8.4 g/cm^3, respectively.

Solution

The value of N_{Cu}—the number of atomic sites per cubic meter for copper, from its atomic weight A_{Cu}, its density ρ, and Avogadro's number N_A, according to

$$\boxed{N_{\mathrm{Cu}} = \frac{N_A \rho}{A_{\mathrm{Cu}}}}$$

$$= \frac{(6.022 \times 10^{23}\ \text{atoms/mol})(8.4\ \text{g/cm}^3)(10^6\ \text{cm}^3/\text{m}^3)}{63.5\ \text{g/mol}}$$

$$= 8.0 \times 10^{28}\ \text{atoms/m}^3$$

Thus, the number of vacancies at 1000°C (1273 K) is equal to

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

$$= (8.0 \times 10^{28}\ \text{atoms/m}^3) \exp\left[-\frac{(0.9\ \text{eV})}{(8.62 \times 10^{-5}\ \text{eV/K})(1273\ \text{K})}\right]$$

$$= 2.2 \times 10^{25}\ \text{vacancies/m}^3$$

IMPURITIES IN SOLIDS

A pure metal consisting of only one type of atom just isn’t possible; impurity or foreign atoms are always present, and some exist as crystalline point defects.

In fact, even with relatively sophisticated techniques, it is difficult to refine metals to a purity in excess of 99.9999%. At this level, on the order of 10^{22} to 10^{23} impurity atoms are present in 1 m^3 of material.

Most familiar metals are not highly pure; rather, they are **alloys,** in which impurity atoms have been added intentionally to impart specific characteristics to the material. Ordinarily, alloying is used in metals to improve mechanical strength and corrosion resistance.

For example, sterling silver is a 92.5% silver–7.5% copper alloy. In normal ambient environments, pure silver is highly corrosion resistant, but also very soft. Alloying with copper significantly enhances the mechanical strength without reducing the corrosion resistance appreciably.

The addition of impurity atoms to a metal results in the formation of a **solid solution** and/or a new *second phase*, depending on the kinds of impurity, their concentrations, and the temperature of the alloy.

Several terms relating to impurities and solid solutions deserve mention. With regard to alloys, **solute** and **solvent** are terms that are commonly employed. *Solvent* is the element or compound that is present in the greatest amount; on occasion, solvent atoms are also called *host atoms*. *Solute* is used to denote an element or compound present in a minor concentration.

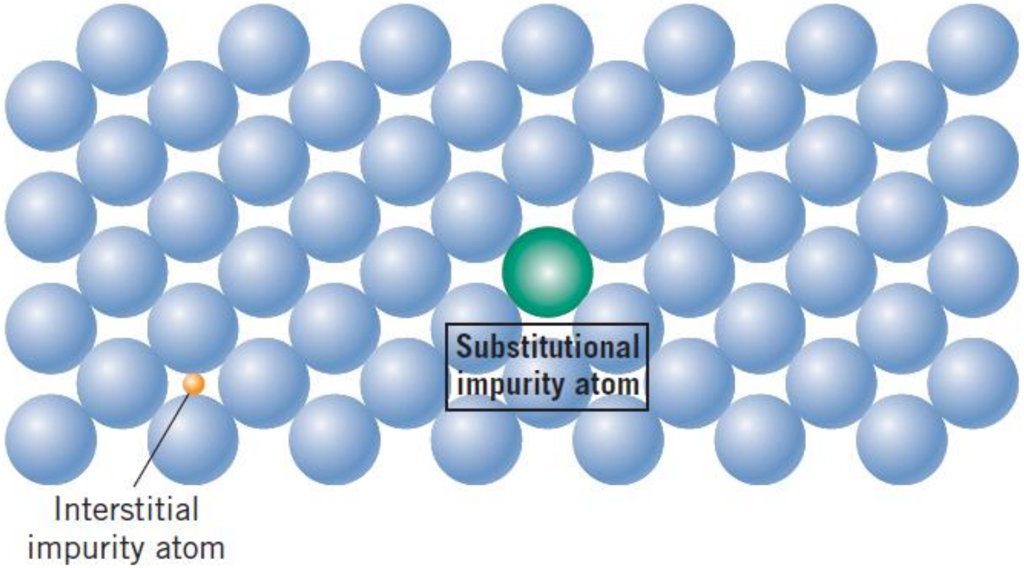
IMPURITIES IN SOLIDS

Solid Solutions

A solid solution forms when, as the solute atoms are added to the host material, the crystal structure is maintained and no new structures are formed. Perhaps it is useful to draw an analogy with a liquid solution. If two liquids that are soluble in each other (such as water and alcohol) are combined, a liquid solution is produced as the molecules intermix, and its composition is homogeneous throughout.

A solid solution is also compositionally homogeneous; the impurity atoms are randomly and uniformly dispersed within the solid.

Impurity point defects are found in solid solutions, of which there are two types: **substitutional** and **interstitial.** For the substitutional type, solute or impurity atoms replace or substitute for the host atoms.



Two-dimensional schematic representations of substitutional and interstitial impurity atoms.

IMPURITIES IN SOLIDS

Several features of the solute and solvent atoms determine the degree to which the former dissolves in the latter.

These are expressed as four *Hume–Rothery rules*, as follows:

1. *Atomic size factor*. Appreciable quantities of a solute may be accommodated in this type of solid solution only when the difference in atomic radii between the two atom types is less than about ±15%. Otherwise, the solute atoms create substantial lattice distortions and a new phase forms.
2. *Crystal structure*. For appreciable solid solubility, the crystal structures for metals of both atom types must be the same.
3. *Electronegativity factor*. The more electropositive one element and the more electronegative the other, the greater the likelihood that they will form an intermetallic compound instead of a substitutional solid solution.
4. *Valences*. Other factors being equal, a metal has more of a tendency to dissolve another metal of higher valency than to dissolve one of a lower valency.

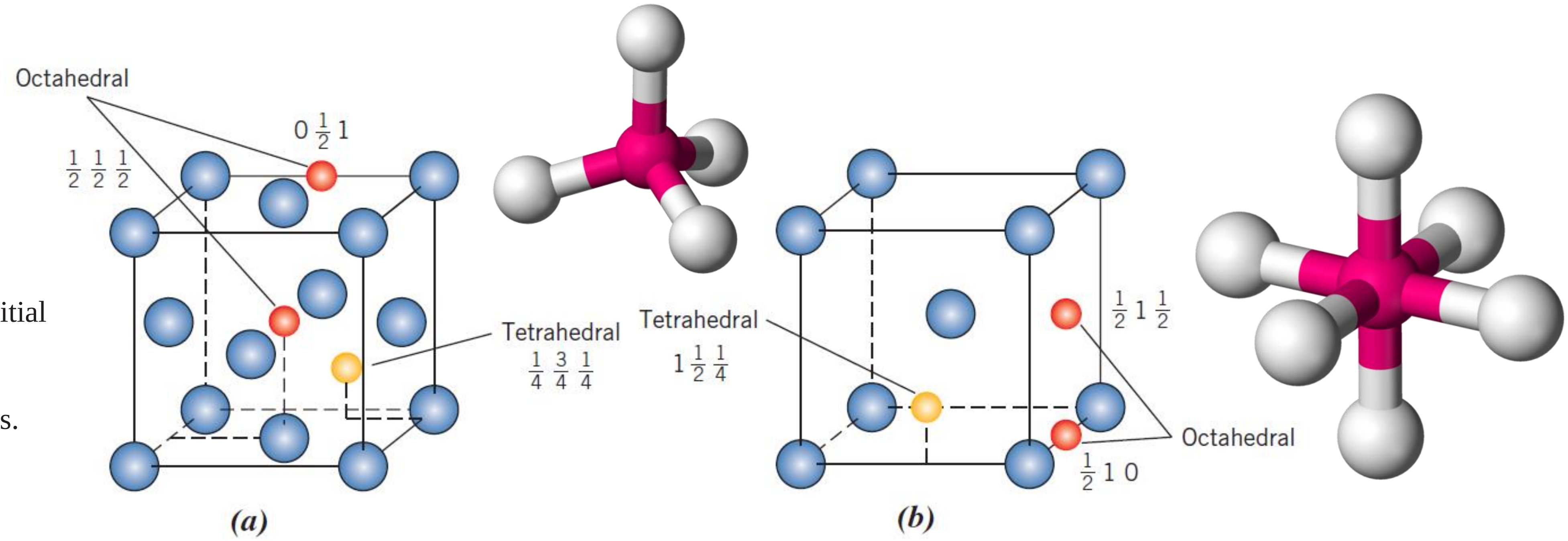
An example of a substitutional solid solution is found for copper and nickel. These two elements are completely soluble in one another at all proportions.

With regard to the aforementioned rules that govern degree of solubility, the atomic radii for copper and nickel are 0.128 and 0.125 nm, respectively; both have the FCC crystal structure; and their electronegativities are 1.9 and 1.8. Finally, the most common valences are +1 for copper (although it sometimes can be +2) and +2 for nickel.

IMPURITIES IN SOLIDS

For interstitial solid solutions, impurity atoms fill the voids or interstices among the host atoms. For both FCC and BCC crystal structures, there are two types of interstitial sites—*tetrahedral* and *octahedral;* these are distinguished by the number of nearest neighbour host atoms—that is, the coordination number.

Tetrahedral sites have a coordination number of 4; straight lines drawn from the centres of the surrounding host atoms form a four-sided tetrahedron.



Locations of tetrahedral and octahedral interstitial sites within (*a*) FCC and (*b*) BCC unit cells.

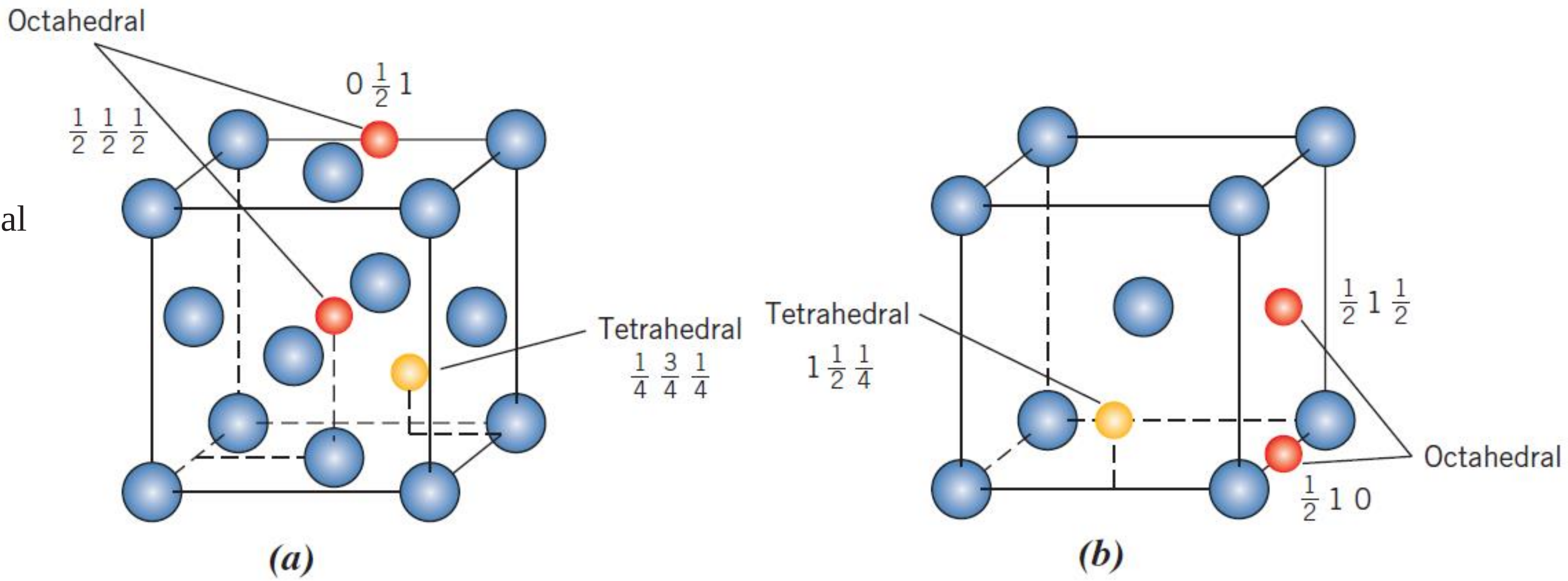
IMPURITIES IN SOLIDS

However, for octahedral sites the coordination number is 6; an octahedron is produced by joining these six sphere centers. For FCC, there are two types of octahedral sites with representative point coordinates of $0\frac{1}{2}1$ and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$.

Representative coordinates for a single tetrahedral site type are $\frac{1}{4}\frac{3}{4}\frac{1}{4}$. Locations of these sites within the FCC unit cell are noted in Figure *a*. Likewise, for BCC, there are two octahedral and one tetrahedral types. Representative coordinates for the octahedral sites are as follows: $\frac{1}{2}1\frac{1}{2}$ and $\frac{1}{2}1\,0$; for BCC tetrahedral, $1\frac{1}{2}\frac{1}{4}$ is a representative coordinate.

Figure *b* shows the positions of these sites within a BCC unit cell.

Locations of tetrahedral and octahedral interstitial sites within
(*a*) FCC and
(*b*) BCC unit cells.



IMPURITIES IN SOLIDS

Metallic materials have relatively high atomic packing factors, which means that these interstitial positions are relatively small. Consequently, the atomic diameter of an interstitial impurity must be substantially smaller than that of the host atoms.

Normally, the maximum allowable concentration of interstitial impurity atoms is low (less than 10%). Even very small impurity atoms are ordinarily larger than the interstitial sites, and as a consequence, they introduce some lattice strains on the adjacent host atoms.

Carbon forms an interstitial solid solution when added to iron; the maximum concentration of carbon is about 2%. The atomic radius of the carbon atom is much less than that of iron: 0.071 nm versus 0.124 nm.

IMPURITIES IN SOLIDS

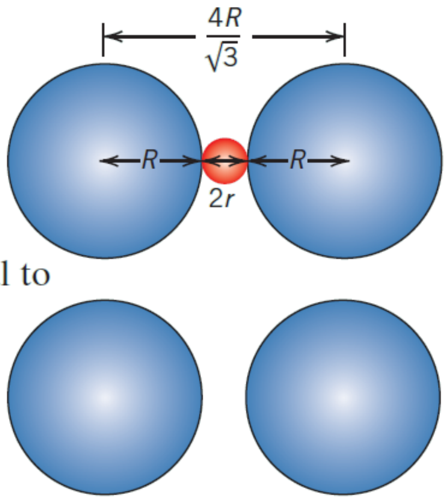
EXAMPLE

Computation of Radius of BCC Interstitial Site

Compute the radius r of an impurity atom that just fits into a BCC octahedral site in terms of the atomic radius R of the host atom (without introducing lattice strains).

Solution

For BCC, one octahedral interstitial site is situated at the center of a unit cell edge. In order for an interstitial atom to be positioned in this site without introducing lattice strains, the atom just touches the two adjacent host atoms, which are corner atoms of the unit cell. The drawing shows atoms on the (100) face of a BCC unit cell; the large circles represent the host atoms—the small circle represents an interstitial atom that is positioned in an octahedral site on the cube edge.



On this drawing is noted the unit cell edge length—the distance between the centers of the corner atoms—which, is equal to

$$\text{Unit cell edge length} = \frac{4R}{\sqrt{3}}$$

Also shown is that the unit cell edge length is equal to two times the sum of host atomic radius $2R$ plus twice the radius of the interstitial atom $2r$; i.e.,

$$\text{Unit cell edge length} = 2R + 2r$$

Now, equating these two unit cell edge length expressions, we get

$$2R + 2r = \frac{4R}{\sqrt{3}}$$

and solving for r in terms of R

$$2r = \frac{4R}{\sqrt{3}} - 2R = \left(\frac{2}{\sqrt{3}} - 1\right)(2R)$$

$$r = \left(\frac{2}{\sqrt{3}} - 1\right)R = 0.155R$$

SPECIFICATION OF COMPOSITION

It is often necessary to express the **composition** (or *concentration*) of an alloy in terms of its constituent elements. The two most common ways to specify composition are weight (or mass) percent and atom percent. The basis for **weight percent** (wt%) is the weight of a particular element relative to the total alloy weight.

For an alloy that contains two hypothetical atoms denoted by 1 and 2, the concentration of 1 in wt%, C_1, is defined as

$$C_1 = \frac{m_1}{m_1 + m_2} \times 100$$

where m_1 and m_2 represent the weight (or mass) of elements 1 and 2, respectively. The concentration of 2 is computed in an analogous manner.

When an alloy contains more than two (say n) elements, then:

$$C_1 = \frac{m_1}{m_1 + m_2 + m_3 + \cdots + m_n} \times 100$$

The basis for **atom percent** (at%) calculations is the number of moles of an element in relation to the total moles of the elements in the alloy. The number of moles in some specified mass of a hypothetical element 1, n_{m1}, may be computed as follows:

$$n_{m1} = \frac{m_1'}{A_1}$$

SPECIFICATION OF COMPOSITION

Here, m'_1 and A_1 denote the mass (in grams) and atomic weight, respectively, for element 1. Concentration in terms of atom percent of element 1 in an alloy containing element 1 and element 2 atoms, C'_1 is defined by:

$$C'_1 = \frac{n_{m1}}{n_{m1} + n_{m2}} \times 100$$

In like manner, the atom percent of element 2 is determined**.**

When an alloy contains more than two (say n) elements, then:

$$C'_1 = \frac{n_{m1}}{n_{m1} + n_{m2} + n_{m3} + \cdots + n_{mn}} \times 100$$

Atom percent computations also can be carried out on the basis of the number of atoms instead of moles, because one mole of all substances contains the same number of atoms.

SPECIFICATION OF COMPOSITION

Composition Conversions

Sometimes it is necessary to convert from one composition scheme to another—for example, from weight percent to atom percent.

Using the convention of the previous section (i.e., weight% denoted by C_1 and C_2, atom% by C'_1 and C'_2, and atomic weights as A_1 and A_2), we express these conversion equations as follows:

$$C'_1 = \frac{C_1A_2}{C_1A_2 + C_2A_1} \times 100 \qquad C'_2 = \frac{C_2A_1}{C_1A_2 + C_2A_1} \times 100$$

$$C_1 = \frac{C'_1A_1}{C'_1A_1 + C'_2A_2} \times 100 \qquad C_2 = \frac{C'_2A_2}{C'_1A_1 + C'_2A_2} \times 100$$

Because we are considering only two elements, computations involving the preceding equations are simplified when it is realized that: $C_1 + C_2 = 100$ and $C'_1 + C'_2 = 100$

In addition, it sometimes becomes necessary to convert concentration from weight percent to mass of one component per unit volume of material (i.e., from units of wt% to kg/m3); this latter composition scheme is often used in diffusion computations. Concentrations in terms of this basis are denoted using a double prime (i.e., $C''1$ and $C''2$), and the relevant equations are as follows:

For density ρ in units of g/cm^3, these expressions yield C''_1 and C''_2 in kg/m^3.

$$C''_1 = \left(\frac{C_1}{\frac{C_1}{\rho_1} + \frac{C_2}{\rho_2}}\right) \times 10^3 \qquad C''_2 = \left(\frac{C_2}{\frac{C_1}{\rho_1} + \frac{C_2}{\rho_2}}\right) \times 10^3$$

SPECIFICATION OF COMPOSITION

Furthermore, on occasion we desire to determine the density and atomic weight of a binary alloy, given the composition in terms of either weight percent or atom percent.

If we represent alloy density and atomic weight by ρ_{ave} and A_{ave}, respectively, then:

$$\rho_{\text{ave}} = \frac{100}{\dfrac{C_1}{\rho_1} + \dfrac{C_2}{\rho_2}} = \frac{C_1'A_1 + C_2'A_2}{\dfrac{C_1'A_1}{\rho_1} + \dfrac{C_2'A_2}{\rho_2}} \qquad A_{\text{ave}} = \frac{100}{\dfrac{C_1}{A_1} + \dfrac{C_2}{A_2}} = \frac{C_1'A_1 + C_2'A_2}{100}$$

It should be noted that are not always exact. In their derivations, it is assumed that total alloy volume is exactly equal to the sum of the volumes of the individual elements.

This normally is not the case for most alloys; however, it is a reasonably valid assumption and does not lead to significant errors for dilute solutions and over composition ranges where solid solutions exist.

SPECIFICATION OF COMPOSITION

EXAMPLE

Composition Conversion—From Weight Percent to Atom Percent

Determine the composition, in atom percent, of an alloy that consists of 97 wt% aluminum and 3 wt% copper.

Solution

If we denote the respective weight percent compositions as $C_{\mathrm{Al}} = 97$ and $C_{\mathrm{Cu}} = 3$, substitution yields

$$\begin{aligned} C'_{\mathrm{Al}} &= \frac{C_{\mathrm{Al}}A_{\mathrm{Cu}}}{C_{\mathrm{Al}}A_{\mathrm{Cu}} + C_{\mathrm{Cu}}A_{\mathrm{Al}}} \times 100 \\ &= \frac{(97)(63.55\ \mathrm{g/mol})}{(97)(63.55\ \mathrm{g/mol}) + (3)(26.98\ \mathrm{g/mol})} \times 100 \\ &= 98.7\ \mathrm{at\%} \end{aligned}$$

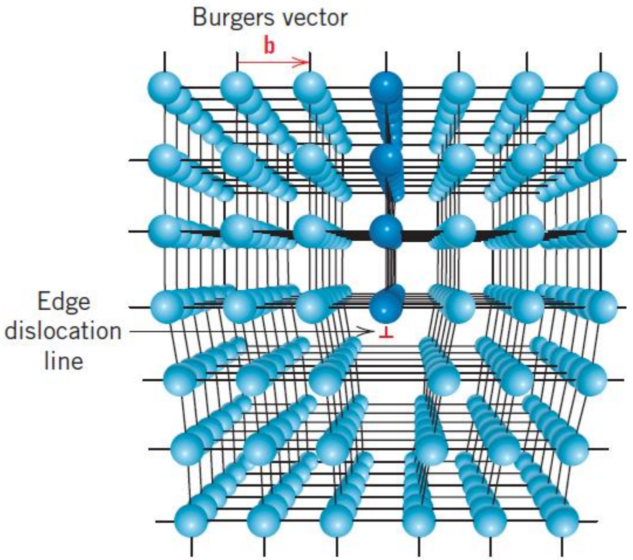
and

$$\begin{aligned} C'_{\mathrm{Cu}} &= \frac{C_{\mathrm{Cu}}A_{\mathrm{Al}}}{C_{\mathrm{Cu}}A_{\mathrm{Al}} + C_{\mathrm{Al}}A_{\mathrm{Cu}}} \times 100 \\ &= \frac{(3)(26.98\ \mathrm{g/mol})}{(3)(26.98\ \mathrm{g/mol}) + (97)(63.55\ \mathrm{g/mol})} \times 100 \\ &= 1.30\ \mathrm{at\%} \end{aligned}$$

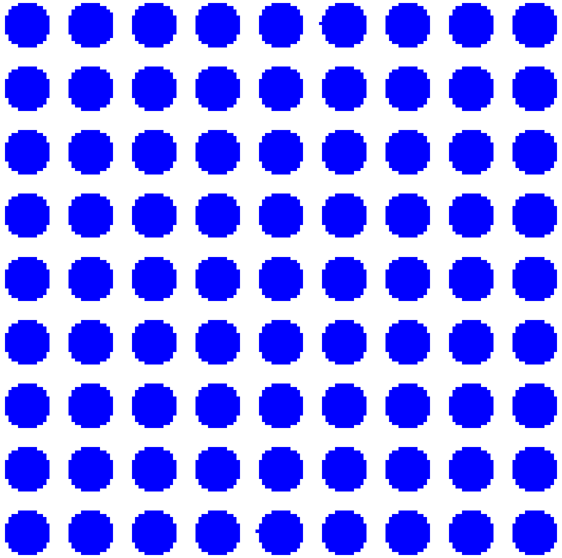
MISCELLANEOUS IMPERFECTIONS

A *dislocation* is a linear or one-dimensional defect around which some of the atoms are misaligned. One type of dislocation is represented: an extra portion of a plane of atoms, or half-plane, the edge of which terminates within the crystal.

This is termed an **edge dislocation;** it is a linear defect that centres on the line that is defined along the end of the extra half-plane of atoms. This is sometimes termed the **dislocation line,** which, for the edge dislocation in the figure, is perpendicular to the plane of the page.

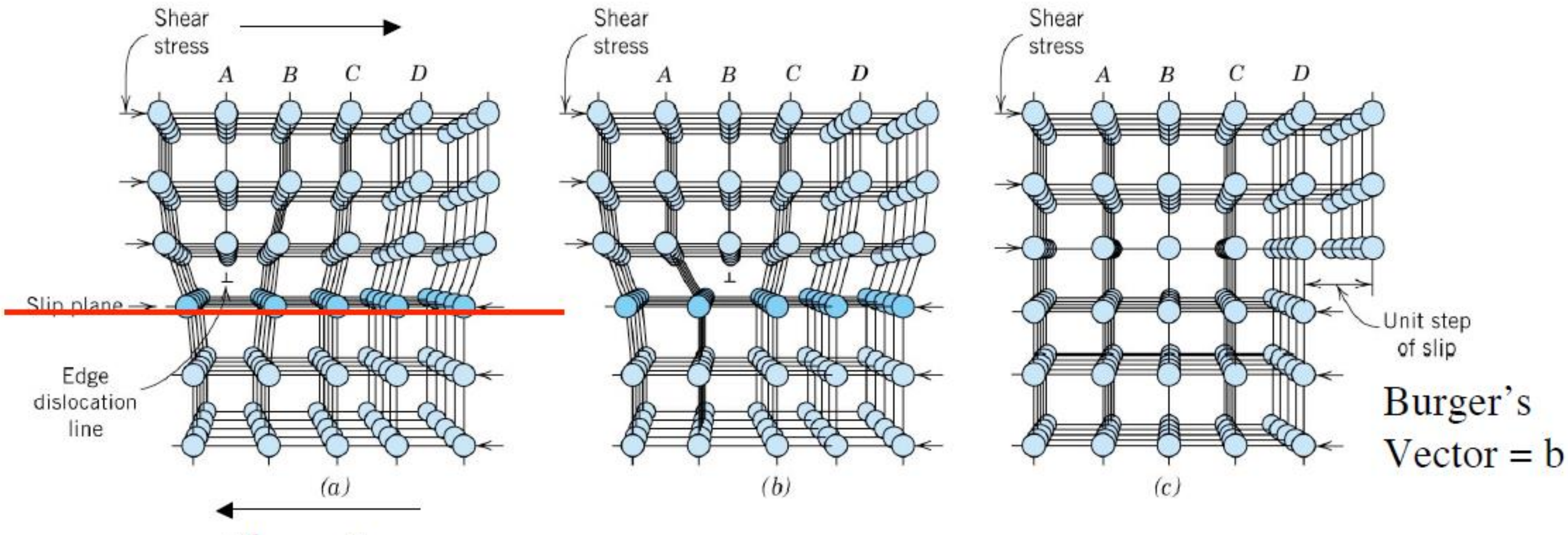


The atom positions around an edge dislocation; extra half-plane of atoms shown in perspective.



Burger’s vectors mostly on the most close-packed planes in the most closed-packed direction.

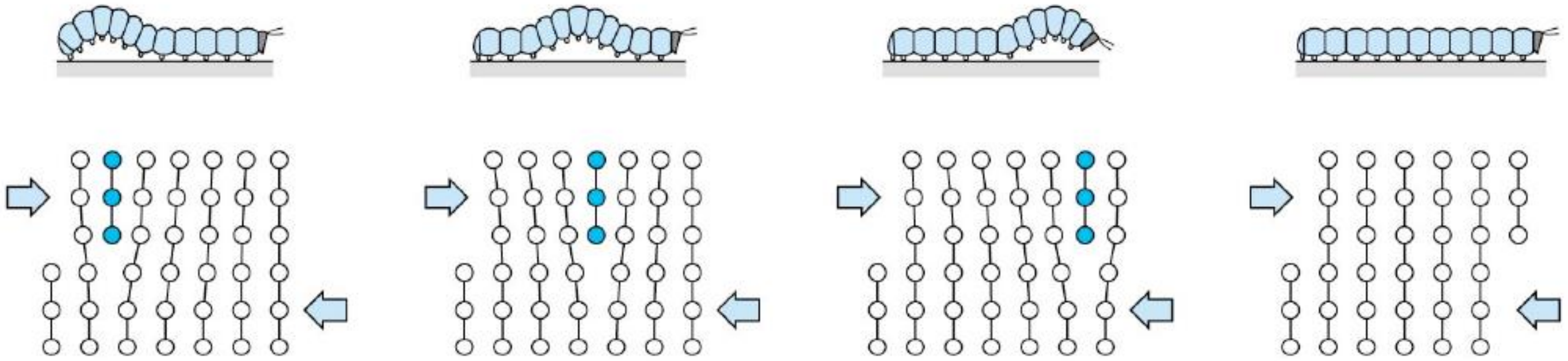
MISCELLANEOUS IMPERFECTIONS



Burger's Vector = b

Shear stress

The caterpillar or rug-moving analogy



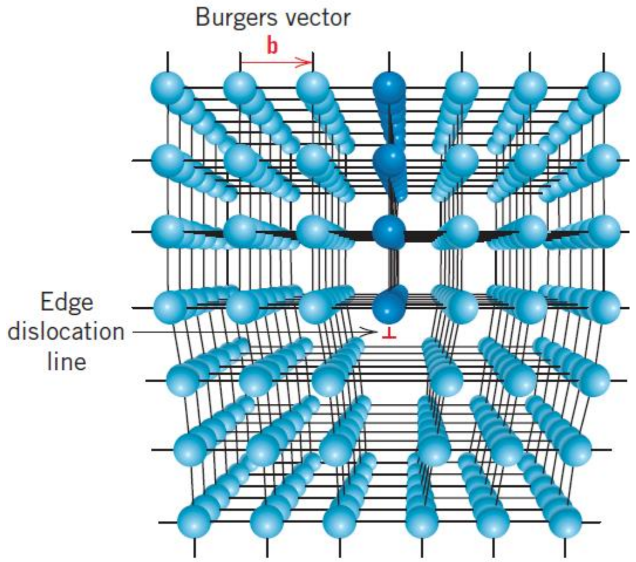
MISCELLANEOUS IMPERFECTIONS

Within the region around the dislocation line there is some localized lattice distortion.

The atoms above the dislocation line are squeezed together, and those below are pulled apart; this is reflected in the slight curvature for the vertical planes of atoms as they bend around this extra half-plane.

The magnitude of this distortion decreases with distance away from the dislocation line; at positions far removed, the crystal lattice is virtually perfect. Sometimes the edge dislocation is represented by the symbol ⊥, which also indicates the position of the dislocation line.

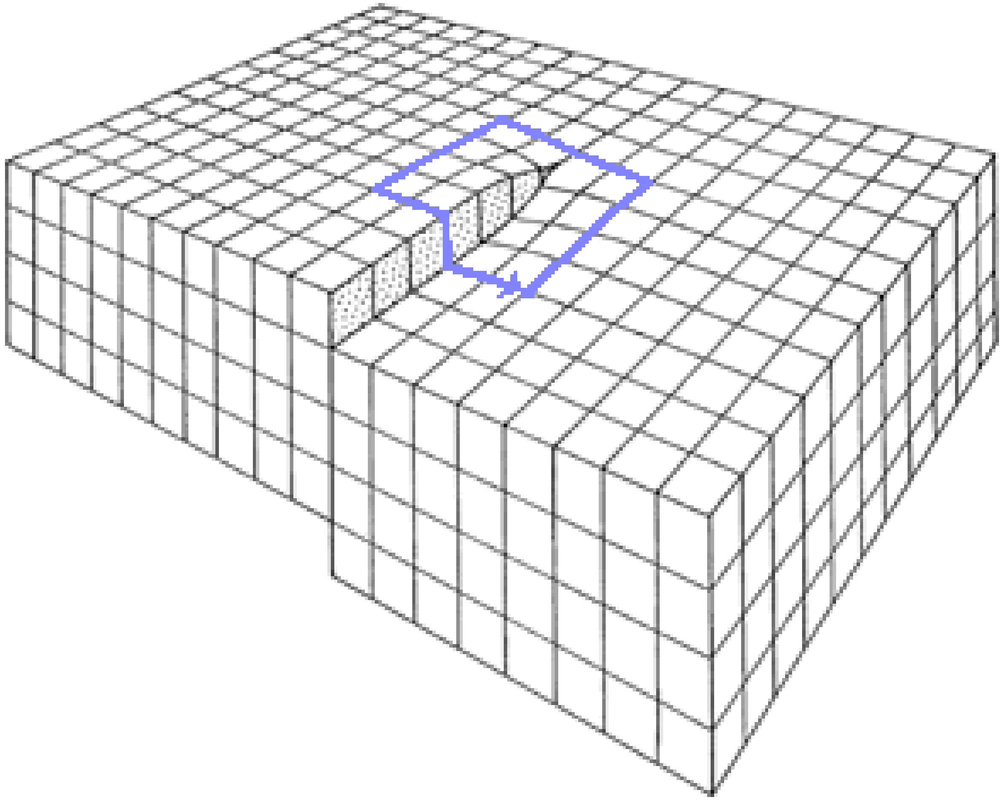
An edge dislocation may also be formed by an extra halfplane of atoms that is included in the bottom portion of the crystal; its designation is a ⊤.



The atom positions around an edge dislocation; extra half-plane of atoms shown in perspective.

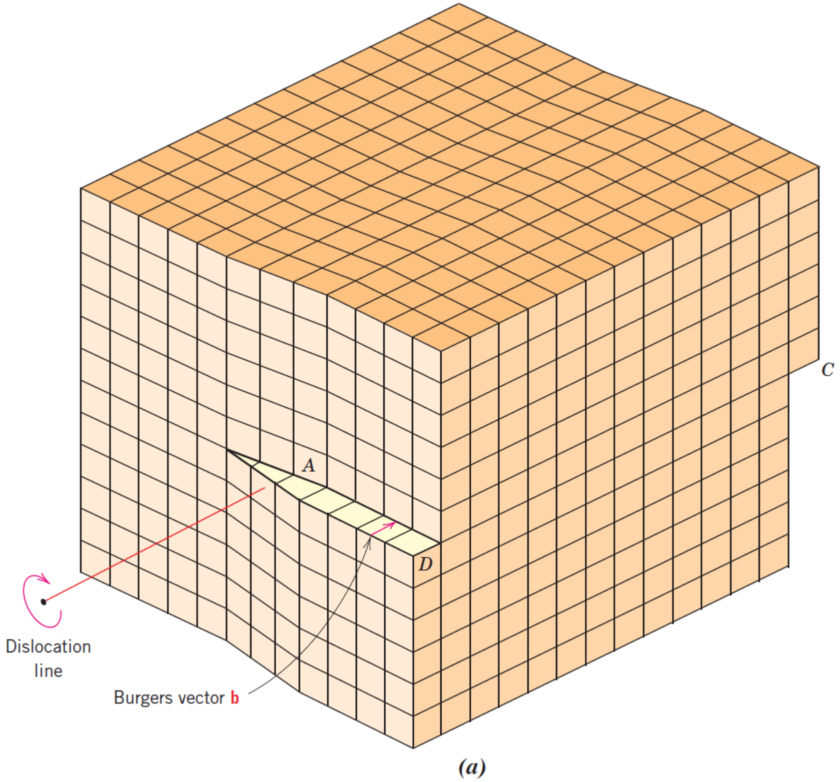
MISCELLANEOUS IMPERFECTIONS

Another type of dislocation, called a **screw dislocation,** may be thought of as being formed by a shear stress that is applied to produce the distortion shown:



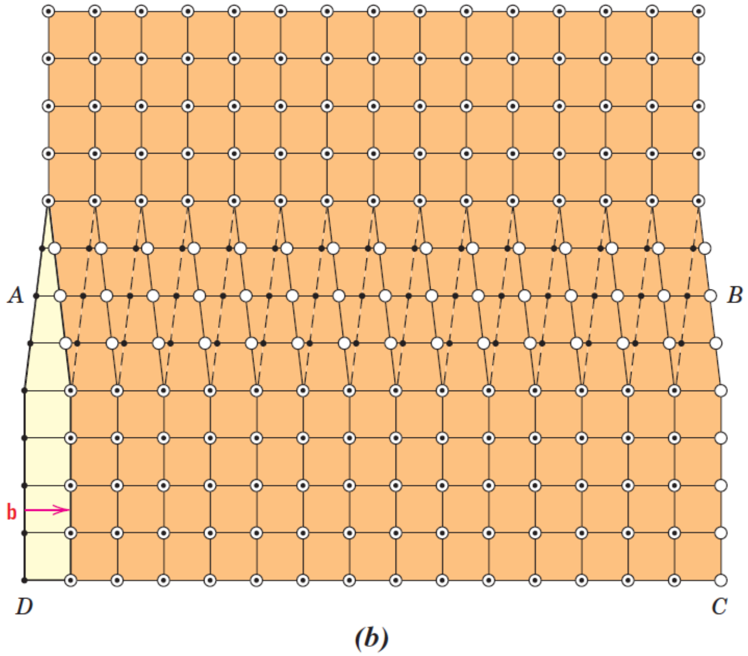
MISCELLANEOUS IMPERFECTIONS

Another type of dislocation, called a **screw dislocation,** may be thought of as being formed by a shear stress that is applied to produce the distortion shown:



(*a*) A screw dislocation within a crystal.
(*b*) The screw dislocation in (*a*) as viewed from above.

The dislocation line extends along line *AB*. Atom positions above the slip plane are designated by open circles, those below by solid circles.

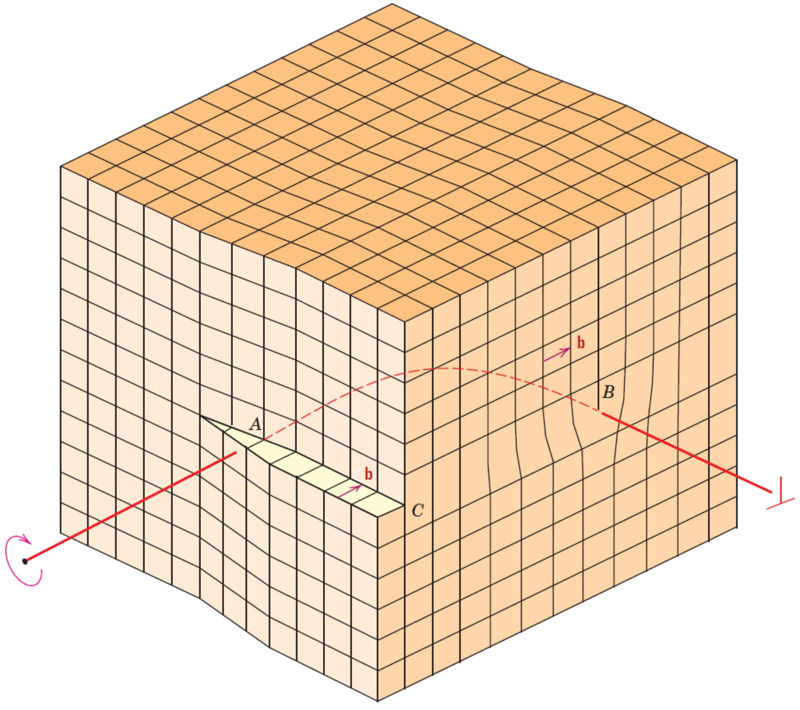


The upper front region of the crystal is shifted one atomic distance to the right relative to the bottom portion. The atomic distortion associated with a screw dislocation is also linear and along a dislocation line, line *AB* in Figure *b*. The screw dislocation derives its name from the spiral or helical path or ramp that is traced around the dislocation line by the atomic planes of atoms. Sometimes the symbol ↻ is used to designate a screw dislocation.

MISCELLANEOUS IMPERFECTIONS

Most dislocations found in crystalline materials are probably neither pure edge nor pure screw but exhibit components of both types; these are termed **mixed dislocations.**

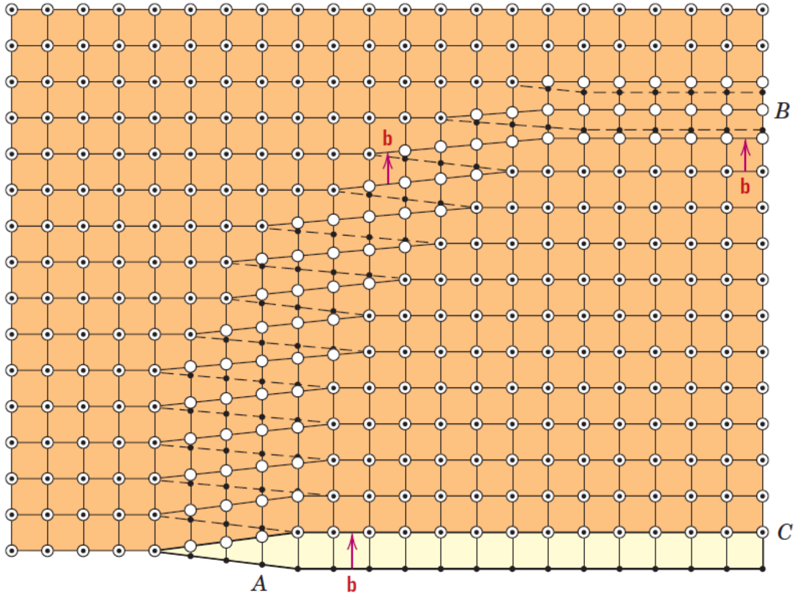
All three dislocation types are represented schematically; the lattice distortion that is produced away from the two faces is mixed, having varying degrees of screw and edge character.



(a)

- (a) Schematic representation of a dislocation that has edge, screw, and mixed character.
- (b) Top view, where open circles denote atom positions above the slip plane, and solid circles, atom positions below.

At point *A*, the dislocation is pure screw, while at point *B*, it is pure edge. For regions in between where there is curvature in the dislocation line, the character is mixed edge and screw.



(b)

MISCELLANEOUS IMPERFECTIONS

The magnitude and direction of the lattice distortion associated with a dislocation are expressed in terms of a **Burgers vector,** denoted by **b**.

The nature of a dislocation (i.e., edge, screw, or mixed) is defined by the relative orientations of dislocation line and Burgers vector. For an edge, they are perpendicular, whereas for a screw, they are parallel; they are neither perpendicular nor parallel for a mixed dislocation.

Also, even though a dislocation changes direction and nature within a crystal (e.g., from edge to mixed to screw), the Burgers vector is the same at all points along its line.

For metallic materials, the Burgers vector for a dislocation points in a close-packed crystallographic direction and is of magnitude equal to the interatomic spacing. The permanent deformation of most crystalline materials is by the motion of dislocations.

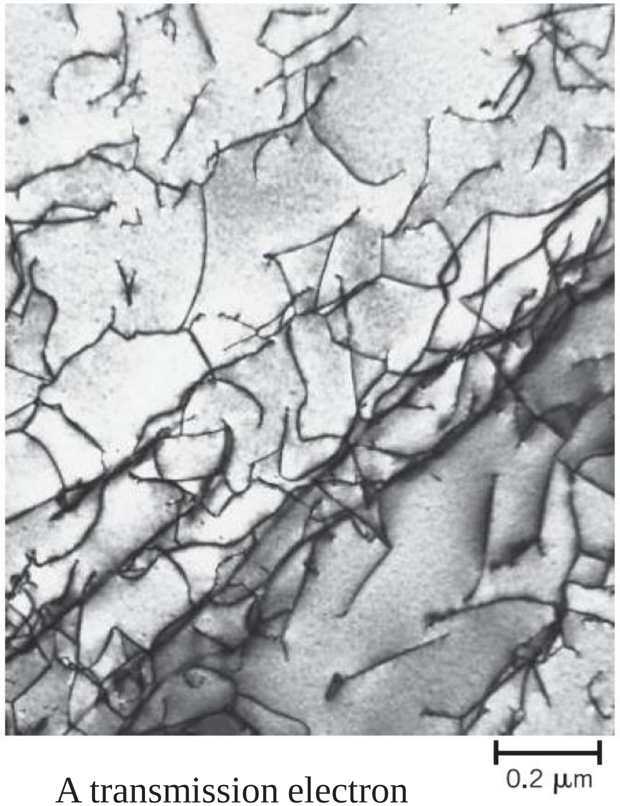
In addition, the Burgers vector is an element of the theory that has been developed to explain this type of deformation.

MISCELLANEOUS IMPERFECTIONS

Dislocations can be observed in crystalline materials using electron-microscopic techniques. A high-magnification transmission electron micrograph is shown, the dark lines are the dislocations.

Virtually all crystalline materials contain some dislocations that were introduced during solidification, during plastic deformation, and as a consequence of thermal stresses that result from rapid cooling.

Dislocations are involved in the plastic deformation of crystalline materials, both metals and ceramics.



A transmission electron micrograph of a titanium alloy in which the dark lines are dislocations, 50,000×.

INTERFACIAL DEFECTS

Interfacial defects are boundaries that have two dimensions and normally separate regions of the materials that have different crystal structures and/or crystallographic orientations. These imperfections include external surfaces, grain boundaries, phase boundaries, twin boundaries, and stacking faults.

External Surfaces

One of the most obvious boundaries is the external surface, along which the crystal structure terminates. Surface atoms are not bonded to the maximum number of nearest neighbours and are therefore in a higher energy state than the atoms at interior positions.

The bonds of these surface atoms that are not satisfied give rise to a surface energy, expressed in units of energy per unit area (J/m^2 or erg/cm^2).

To reduce this energy, materials tend to minimize, if at all possible, the total surface area. For example, liquids assume a shape having a minimum area—the droplets become spherical. Of course, this is not possible with solids, which are mechanically rigid.

INTERFACIAL DEFECTS

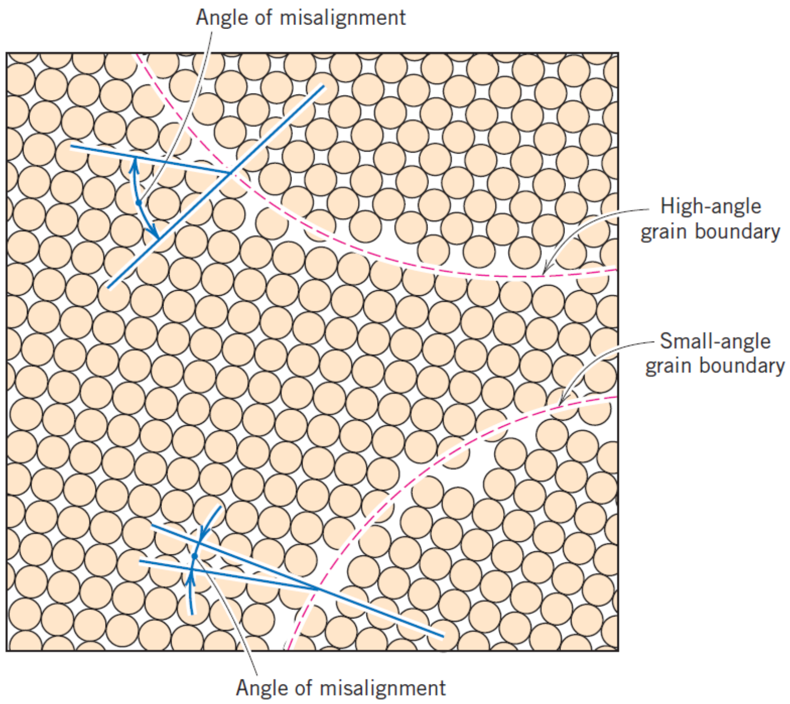
Grain Boundaries

Another interfacial defect, the grain boundary, was introduced as the boundary separating two small grains or crystals having different crystallographic orientations in polycrystalline materials.

A grain boundary is represented schematically from an atomic perspective. Within the boundary region, which is probably just several atom distances wide, there is some atomic mismatch in a transition from the crystalline orientation of one grain to that of an adjacent one.

Various degrees of crystallographic misalignment between adjacent grains are possible. When this orientation mismatch is slight, on the order of a few degrees, then the term *small*- (or *low*-) *angle grain boundary* is used.

These boundaries can be described in terms of dislocation arrays.



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

INTERFACIAL DEFECTS

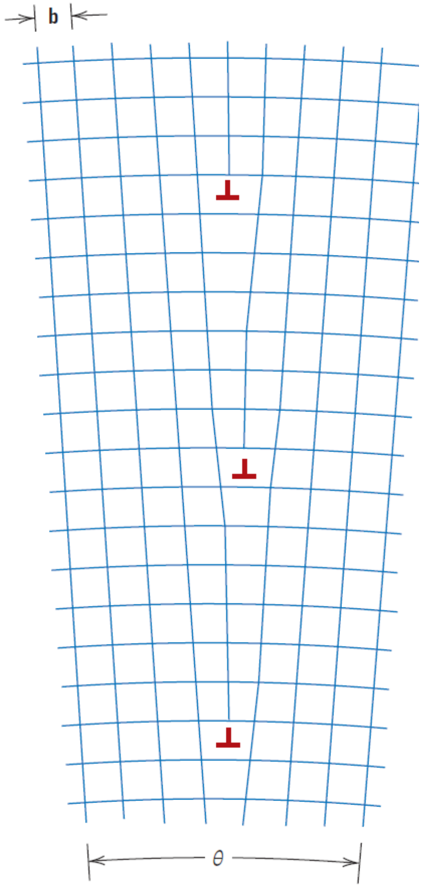
One simple small-angle grain boundary is formed when edge dislocations are aligned in the manner as shown.

This type is called a *tilt boundary;* the angle of misorientation, θ, is also indicated in the figure.

When the angle of misorientation is parallel to the boundary, a *twist boundary* results, which can be described by an array of screw dislocations.

The atoms are bonded less regularly along a grain boundary (e.g., bond angles are longer), and consequently there is an interfacial or grain boundary energy similar to the surface energy just described.

The magnitude of this energy is a function of the degree of misorientation, being larger for high-angle boundaries. Grain boundaries are more chemically reactive than the grains themselves as a consequence of this boundary energy.



Demonstration of how a tilt boundary having an angle of misorientation θ results from an alignment of edge dislocations.

INTERFACIAL DEFECTS

Impurity atoms often preferentially segregate along these boundaries because of their higher energy state. The total interfacial energy is lower in large or coarse-grained materials than in fine-grained ones because there is less total boundary area in the former.

Grains grow at elevated temperatures to reduce the total boundary energy. In spite of this disordered arrangement of atoms and lack of regular bonding along grain boundaries, a polycrystalline material is still very strong; cohesive forces within and across the boundary are present.

Furthermore, the density of a polycrystalline specimen is virtually identical to that of a single crystal of the same material.

Phase Boundaries

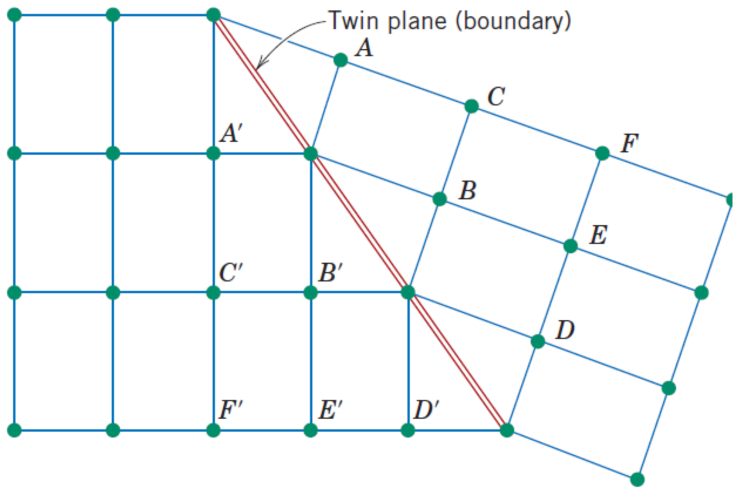
Phase boundaries exist in multiphase materials, in which a different phase exists on each side of the boundary; In addition, each of the constituent phases has its own distinctive physical and/or chemical characteristics.

Phase boundaries play an important role in determining the mechanical characteristics of some multiphase metal alloys.

INTERFACIAL DEFECTS

Twin Boundaries

A *twin boundary* is a special type of grain boundary across which there is a specific mirror lattice symmetry; that is, atoms on one side of the boundary are located in mirror-image positions to those of the atoms on the other side.



Schematic diagram showing a twin plane or boundary and the adjacent atom positions (coloured circles).

Atoms labelled with corresponding primed and unprimed letters (e.g., *A* and *A*′) reside in mirror-imaged positions across the twin boundary.

The region of material between these boundaries is appropriately termed a *twin*. Twins result from atomic displacements that are produced from applied mechanical shear forces (mechanical twins) and also during annealing heat treatments following deformation (annealing twins).

INTERFACIAL DEFECTS

Twinning occurs on a definite crystallographic plane and in a specific direction, both of which depend on the crystal structure.

Annealing twins are typically found in metals that have the FCC crystal structure, whereas mechanical twins are observed in BCC and HCP metals.

Annealing twins may be observed in the photomicrograph of the polycrystalline brass specimen shown. The twins correspond to those regions having relatively straight and parallel sides and a different visual contrast than the untwinned regions of the grains within which they reside.

Miscellaneous Interfacial Defects

Other possible interfacial defects include stacking faults and ferromagnetic domain walls. Stacking faults are found in FCC metals when there is an interruption in the *ABCABCABC* . . . stacking sequence of close-packed planes. For ferromagnetic and ferrimagnetic materials, the boundary that separates regions having different directions of magnetization is termed a *domain wall*.

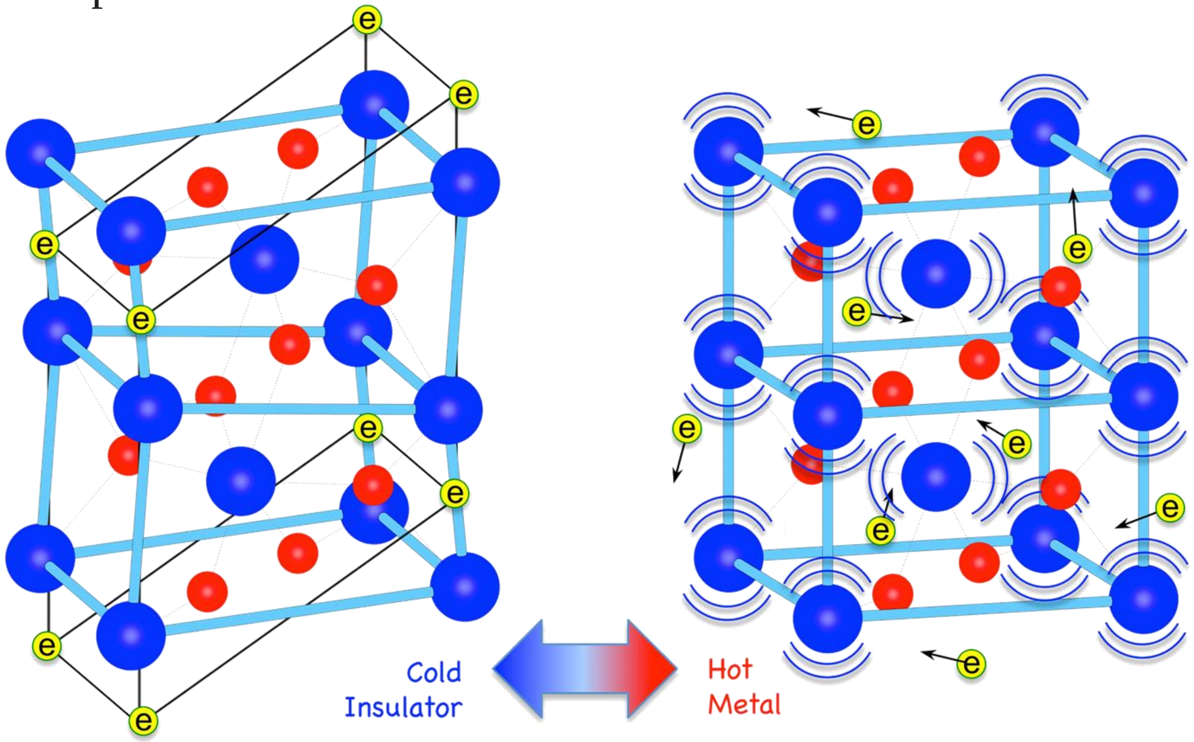
Associated with each of the defects discussed so far is an interfacial energy, the magnitude of which depends on boundary type, and which varies from material to material. Normally, the interfacial energy is greatest for external surfaces and least for domain walls.

BULK OR VOLUME DEFECTS

Other defects exist in all solid materials that are much larger than those heretofore discussed. These include pores, cracks, foreign inclusions, and other phases. They are normally introduced during processing and fabrication steps.

ATOMIC VIBRATIONS

Every atom in a solid material is vibrating very rapidly about its lattice position within the crystal. In a sense, these **atomic vibrations** may be thought of as imperfections or defects.

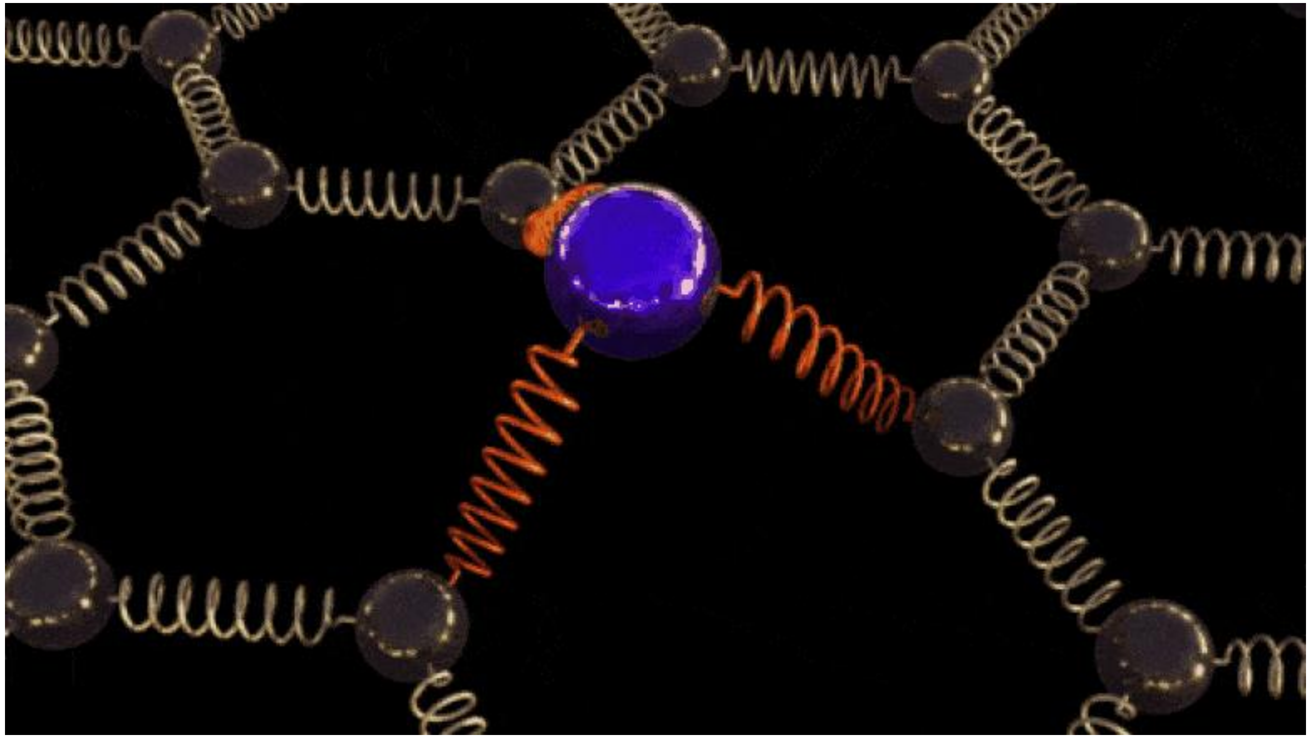


ATOMIC VIBRATIONS

At any instant of time, not all atoms vibrate at the same frequency and amplitude or with the same energy. At a given temperature, there exists a distribution of energies for the constituent atoms about an average energy. Over time, the vibrational energy of any specific atom also varies in a random manner.

With rising temperature, this average energy increases, and, in fact, the temperature of a solid is really just a measure of the average vibrational activity of atoms and molecules. At room temperature, a typical vibrational frequency is on the order of 10^{13} vibrations per second, whereas the amplitude is a few thousandths of a nanometer.

Many properties and processes in solids are manifestations of this vibrational atomic motion. For example, melting occurs when the vibrations are vigorous enough to rupture large numbers of atomic bonds.



MICROSCOPIC EXAMINATION

BASIC CONCEPTS OF MICROSCOPY

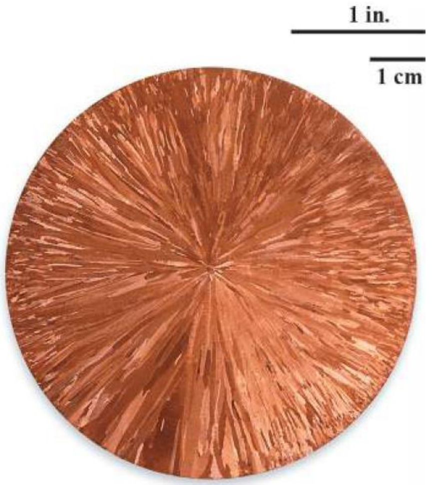
On occasion it is necessary or desirable to examine the structural elements and defects that influence the properties of materials. Some structural elements are of *macroscopic* dimensions; that is, they are large enough to be observed with the unaided eye.

For example, the shape and average size or diameter of the grains for a polycrystalline specimen are important structural characteristics. Macroscopic grains are often evident on aluminium streetlight posts and also on highway guardrails.

Relatively large grains having different textures are clearly visible on the surface of the sectioned copper ingot shown.

However, in most materials the constituent grains are of *microscopic* dimensions, having diameters that may be on the order of microns,10 and their details must be investigated using some type of microscope.

Grain size and shape are only two features of what is termed the **microstructure.**



Cross-section of a cylindrical copper ingot. The small, needle-shape grains may be observed, which extend from the centre radially outward.

MICROSCOPIC EXAMINATION

Optical, electron, and scanning probe microscopes are commonly used in **microscopy.** These instruments aid in investigations of the microstructural features of all material types.

Some of these techniques employ photographic equipment in conjunction with the microscope; the photograph on which the image is recorded is called a **photomicrograph.**

In addition, many microstructural images are computer generated and/or enhanced. Microscopic examination is an extremely useful tool in the study and characterization of materials.

Several important applications of microstructural examinations are:

- to ensure that the associations between the properties and structure (and defects) are properly understood,
- to predict the properties of materials once these relationships have been established,
- to design alloys with new property combinations,
- to determine whether a material has been correctly heat-treated, and
- to ascertain the mode of mechanical fracture.

MICROSCOPIC TECHNIQUES

Optical Microscopy

With *optical microscopy*, the light microscope is used to study the microstructure; optical and illumination systems are its basic elements. For materials that are opaque to visible light (all metals and many ceramics and polymers), only the surface is subject to observation, and the light microscope must be used in a reflecting mode.

Contrasts in the image produced result from differences in reflectivity of the various regions of the microstructure. Investigations of this type are often termed *metallographic* because metals were first examined using this technique.

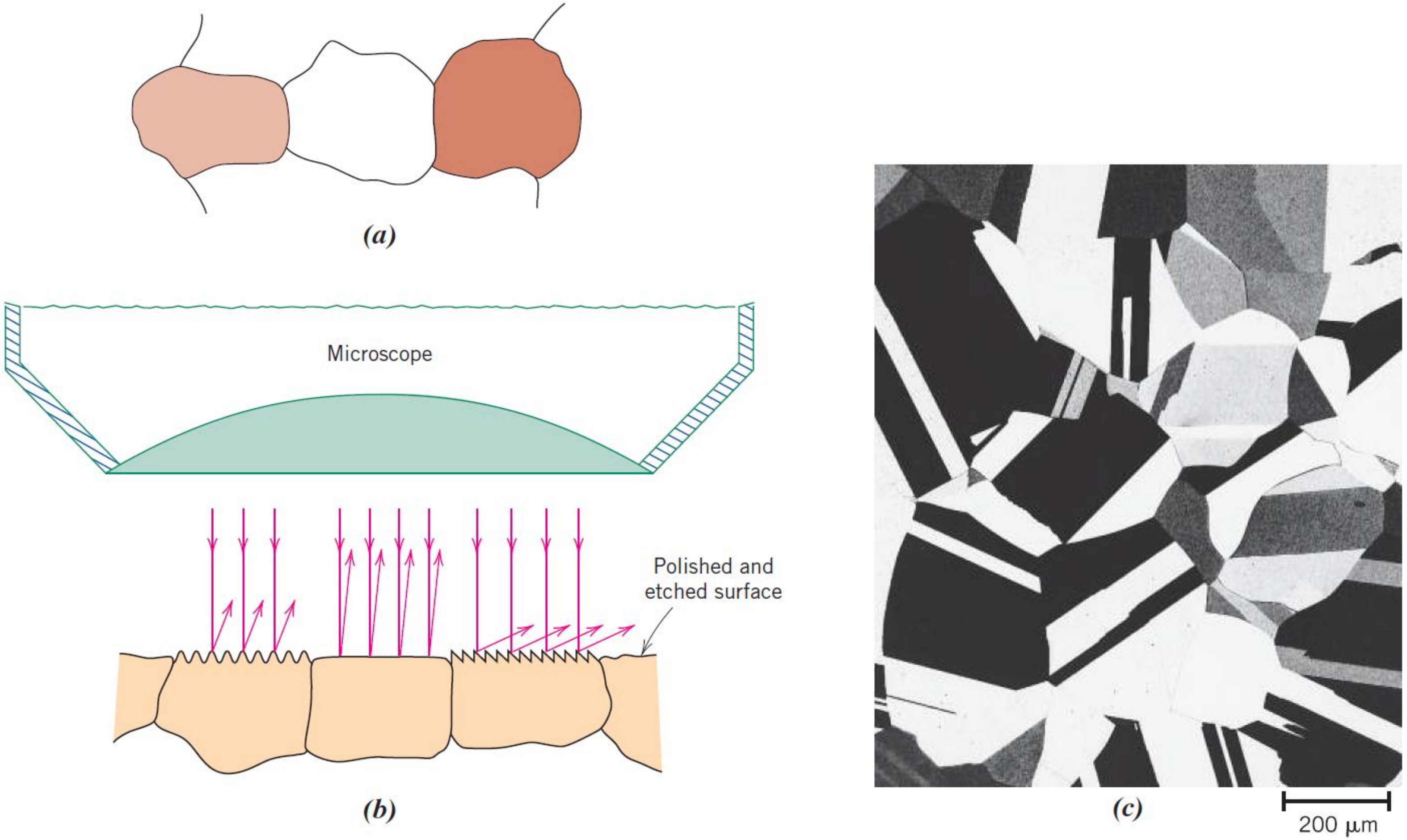
Normally, careful and meticulous surface preparations are necessary to reveal the important details of the microstructure. The specimen surface must first be ground and polished to a smooth and mirror-like finish.

This is accomplished by using successively finer abrasive papers and powders. The microstructure is revealed by a surface treatment using an appropriate chemical reagent in a procedure termed *etching*.

The chemical reactivity of the grains of some single-phase materials depends on crystallographic orientation. Consequently, in a polycrystalline specimen, etching characteristics vary from grain to grain.

MICROSCOPIC TECHNIQUES

Figure *b* shows how normally incident light is reflected by three etched surface grains, each having a different orientation. Figure *a* depicts the surface structure as it might appear when viewed with the microscope; the luster or texture of each grain depends on its reflectance properties. A photomicrograph of a polycrystalline specimen exhibiting these characteristics is shown in Figure *c*.

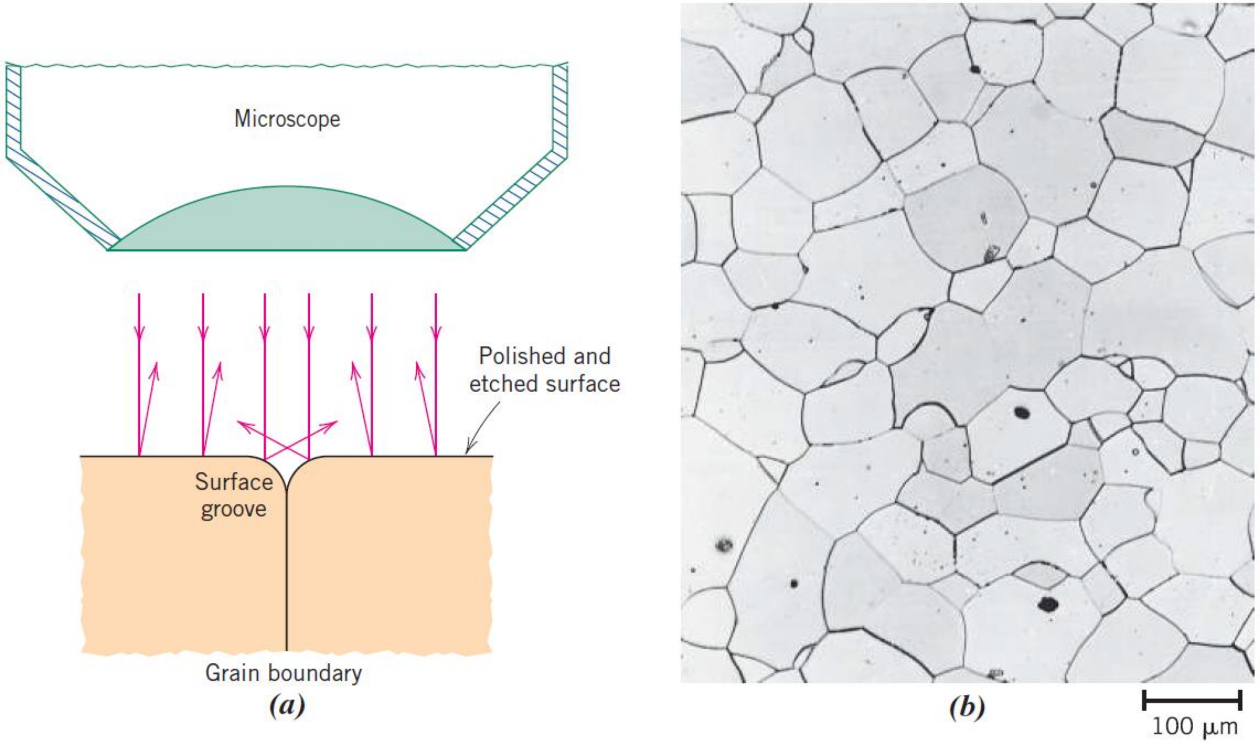


(a) Polished and etched grains as they might appear when viewed with an optical microscope.
(b) Section taken through these grains showing how the etching characteristics and resulting surface texture vary from grain to grain because of differences in crystallographic orientation.
(c) Photomicrograph of a polycrystalline brass specimen, 60×.

MICROSCOPIC TECHNIQUES

Also, small grooves form along grain boundaries as a consequence of etching. Because atoms along grain boundary regions are more chemically active, they dissolve at a greater rate than those within the grains. These grooves become discernible when viewed under a microscope because they reflect light at an angle different from that of the grains themselves; this effect is displayed in Figure *a*. Figure *b* is a photomicrograph of a polycrystalline specimen in which the grain boundary grooves are clearly visible as dark lines.

When the microstructure of a two-phase alloy is to be examined, an etchant is often chosen that produces a different texture for each phase so that the different phases may be distinguished from each other.



(*a*) Section of a grain boundary and its surface groove produced by etching; the light reflection characteristics in the vicinity of the groove are also shown.
(*b*) Photomicrograph of the surface of a polished and etched polycrystalline specimen of an iron–chromium alloy in which the grain boundaries appear dark, 100×.

MICROSCOPIC TECHNIQUES

Electron Microscopy

Some structural elements are too fine or small to permit observation using optical microscopy. The upper limit to the magnification possible with an optical microscope is approximately 2000×.

Under such circumstances, the electron microscope, which is capable of much higher magnifications, may be employed. An image of the structure under investigation is formed using beams of electrons instead of light radiation. According to quantum mechanics, a high-velocity electron becomes wavelike, having a wavelength that is inversely proportional to its velocity.

When accelerated across large voltages, electrons can be made to have wavelengths on the order of 0.003 nm (3 pm). High magnifications and resolving powers of these microscopes are consequences of the short wavelengths of electron beams. The electron beam is focused and the image formed with magnetic lenses; otherwise, the geometry of the microscope components is essentially the same as with optical systems.

Both transmission and reflection beam modes of operation are possible for electron microscopes.

MICROSCOPIC TECHNIQUES

Transmission Electron Microscopy

The image seen with a **transmission electron microscope (TEM)** is formed by an electron beam that passes through the specimen. Details of internal microstructural features are accessible to observation; contrasts in the image are produced by differences in beam scattering or diffraction produced between various elements of the microstructure or defect.

Because solid materials are highly absorptive to electron beams, a specimen to be examined must be prepared in the form of a very thin foil; this ensures transmission through the specimen of an appreciable fraction of the incident beam. The transmitted beam is projected onto a fluorescent screen or a photographic film so that the image may be viewed. Magnifications approaching 1,000,000× are possible with transmission electron microscopy, which is frequently used to study dislocations.

MICROSCOPIC TECHNIQUES

Scanning Electron Microscopy

A more recent and extremely useful investigative tool is the **scanning electron microscope (SEM).** The surface of a specimen to be examined is scanned with an electron beam, and the reflected (or *back-scattered*) beam of electrons is collected and then displayed at the same scanning rate on a cathode ray tube (CRT).

The image on the screen, which may be photographed, represents the surface features of the specimen. The surface may or may not be polished and etched, but it must be electrically conductive; a very thin metallic surface coating must be applied to nonconductive materials. Magnifications ranging from 10× to in excess of 50,000× are possible, as are also very great depths of field. Accessory equipment permits qualitative and semiquantitative analysis of the elemental composition of very localized surface areas.

MICROSCOPIC TECHNIQUES

Scanning Probe Microscopy

In the past two decades, the field of microscopy has experienced a revolution with the development of a new family of scanning probe microscopes.

The **scanning probe microscope (SPM),** of which there are several varieties, differs from optical and electron microscopes in that neither light nor electrons are used to form an image.

Rather, the microscope generates a topographical map, on an atomic scale, that is a representation of surface features and characteristics of the specimen being examined. Some of the features that differentiate the SPM from other microscopic techniques are as follows:

- Examination on the nanometre scale is possible inasmuch as magnifications as high as $10^9\times$ are possible; much better resolutions are attainable than with other microscopic techniques.
- Three-dimensional magnified images are generated that provide topographical information about features of interest.
- Some SPMs may be operated in a variety of environments (e.g., vacuum, air, liquid); thus, a particular specimen may be examined in its most suitable environment.

MICROSCOPIC TECHNIQUES

Scanning probe microscopes employ a tiny probe with a very sharp tip that is brought into very close proximity (i.e., to within on the order of a nanometre) of the specimen surface.

This probe is then raster-scanned across the plane of the surface. During scanning, the probe experiences deflections perpendicular to this plane in response to electronic or other interactions between the probe and specimen surface.

The in-surface-plane and out-of-plane motions of the probe are controlled by piezoelectric ceramic components that have nanometre resolutions.

Furthermore, these probe movements are monitored electronically and transferred to and stored in a computer, which then generates the three-dimensional surface image.

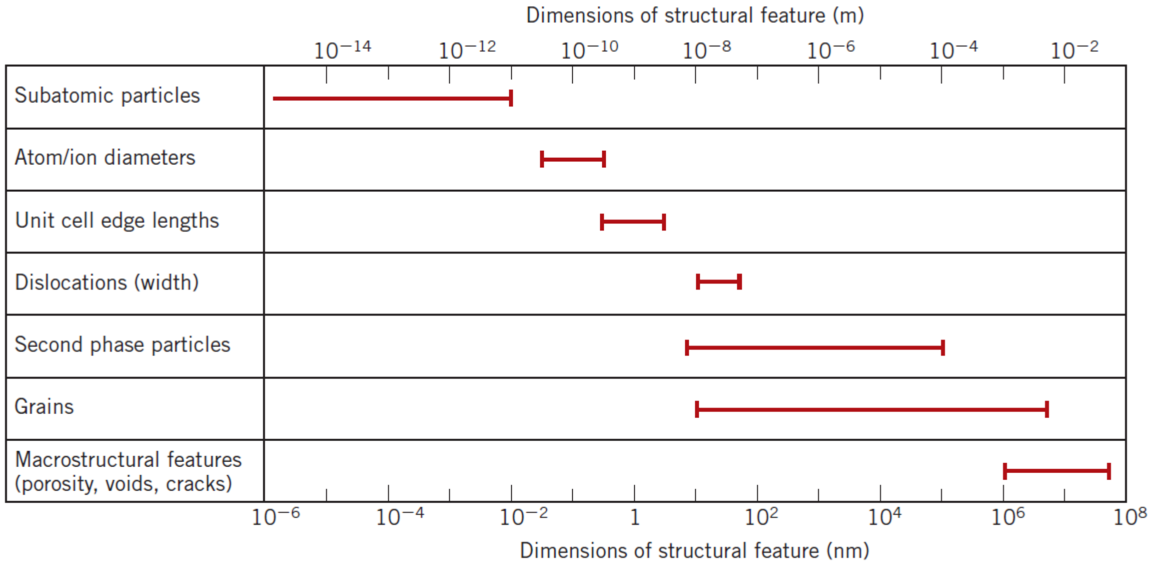
These new SPMs, which allow examination of the surface of materials at the atomic and molecular level, have provided a wealth of information about a host of materials, from integrated circuit chips to biological molecules.

Indeed, the advent of the SPMs has helped to usher in the era of *nanomaterials*—materials whose properties are designed by engineering atomic and molecular structures.

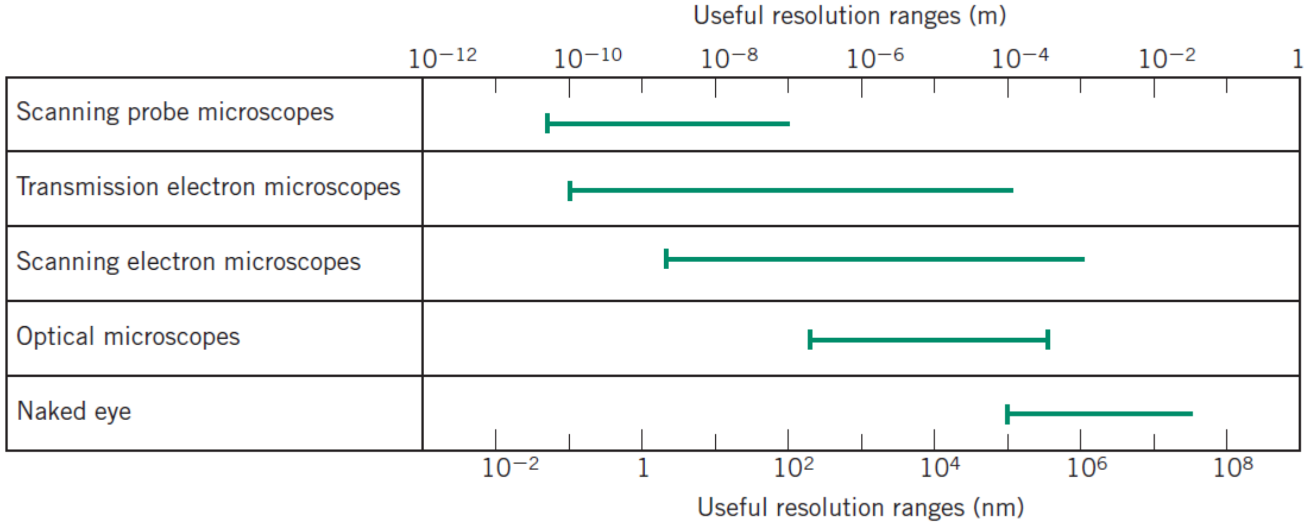
MICROSCOPIC TECHNIQUES

Figure *a* is a bar chart showing dimensional size ranges for several types of structures found in materials (note that the axes are scaled logarithmically). The useful dimensional resolution ranges for the several microscopic techniques (plus the naked eye) are presented in the bar chart of Figure *b*.

For three of these techniques (SPM, TEM, and SEM), an upper resolution value is not imposed by the characteristics of the microscope and, therefore, is somewhat arbitrary and not well defined. Furthermore, by comparing *a* and *b*, it is possible to decide which microscopic technique(s) is (are) best suited for examination of each of the structure types.



(a)



(b)

GRAIN-SIZE DETERMINATION

The **grain size** is often determined when the properties of polycrystalline and single-phase materials are under consideration.

In this regard, it is important to realize that for each material, the constituent grains have a variety of shapes and a distribution of sizes.

Grain size may be specified in terms of average or mean grain diameter, and a number of techniques have been developed to measure this parameter.

Before the advent of the digital age, grain-size determinations were performed manually using photomicrographs. However, today, most techniques are automated and use digital images and image analysers with the capacity to record, detect, and measure accurately features of the grain structure (i.e., grain intercept counts, grain boundary lengths, and grain areas).

There two common grain-size determination techniques:

(1) *linear intercept*—counting numbers of grain boundary intersections by straight test lines; and

(2) *comparison*—comparing grain structures with standardized charts, which are based upon grain areas (i.e., number of grains per unit area).

GRAIN-SIZE DETERMINATION

For the linear intercept method, lines are drawn randomly through several photomicrographs that show the grain structure (all taken at the same magnification).

Grain boundaries intersected by all the line segments are counted. Let us represent the sum of the total number of intersections as P and the total length of all the lines by L_T. The mean intercept length [in real s $\bar{\ell}$ ce (at 1×—i.e., not magnified)], a measure of grain diameter, may be determined by the following expression:

$$\bar{\ell} = \frac{L_T}{PM}$$

where M is the magnification.

The comparison method of grain-size determination was devised by the American Society for Testing and Materials (ASTM). The ASTM has prepared several standard comparison charts, all having different average grain sizes and referenced to photomicrographs taken at a magnification of 100×.

To each chart is assigned a number ranging from 1 to 10, which is termed the *grain-size number*. A specimen must be prepared properly to reveal the grain structure, which is then photographed.

Grain size is expressed as the grain-size number of the chart that most nearly matches the grains in the micrograph. Thus, a relatively simple and convenient visual determination of grain-size number is possible.

Grain-size number is used extensively in the specification of steels.

GRAIN-SIZE DETERMINATION

The rationale behind the assignment of the grain-size number to these various charts is as follows:

Let G represent the grain-size number, and let n be the average number of grains per square inch at a magnification of 100×. These two parameters are related to each other through the expression $n = 2^{G-1}$

For photomicrographs taken at magnifications other than 100×, use of the following modified form of $n = 2^{G-1}$ is necessary:

$$n_M \left(\frac{M}{100}\right)^2 = 2^{G-1}$$

In this expression, n_M is the number of grains per square inch at magnification M. In addition, the inclusion of the $(M/100)^2$ term makes use of the fact that, whereas magnification is a length parameter, area is expressed in terms of units of length squared.

As a consequence, the number of grains per unit area increases with the square of the increase in magnification.

Relationships have been developed that relate mean intercept length to ASTM grain-size number; these are as follows:

$$G = -6.6457 \log \bar{\ell} - 3.298 \qquad (\text{for } \bar{\ell} \text{ in mm})$$

$$G = -6.6353 \log \bar{\ell} - 12.6 \qquad (\text{for } \bar{\ell} \text{ in in.})$$

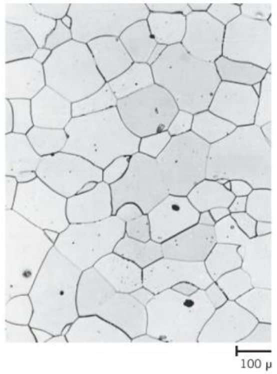
GRAIN-SIZE DETERMINATION

Sometimes magnification is specified in the micrograph legend (60X for example) ; this means the micrograph represents a 60 times enlargement of the specimen in real space.

Scale bars are also used to express degree of magnification. A scale bar is a straight line (typically horizontal), either superimposed on or located near the micrograph image.

Associated with the bar is a length, typically expressed in microns; this value represents the distance in magnified space corresponding to the scale line length.

For example, in the figure, a scale bar is located below the bottom right-hand corner of the micrograph; its “100 μm” notation indicates that 100 μm correlates with the scale bar length.



To compute magnification from a scale bar, the following procedure may be used:

1. Measure the length of the scale bar in millimetres using a ruler.
2. Convert this length into microns [i.e., multiply the value in step (1) by 1000 because there are 1000 microns in a millimetre].
3. Magnification *M* is equal to

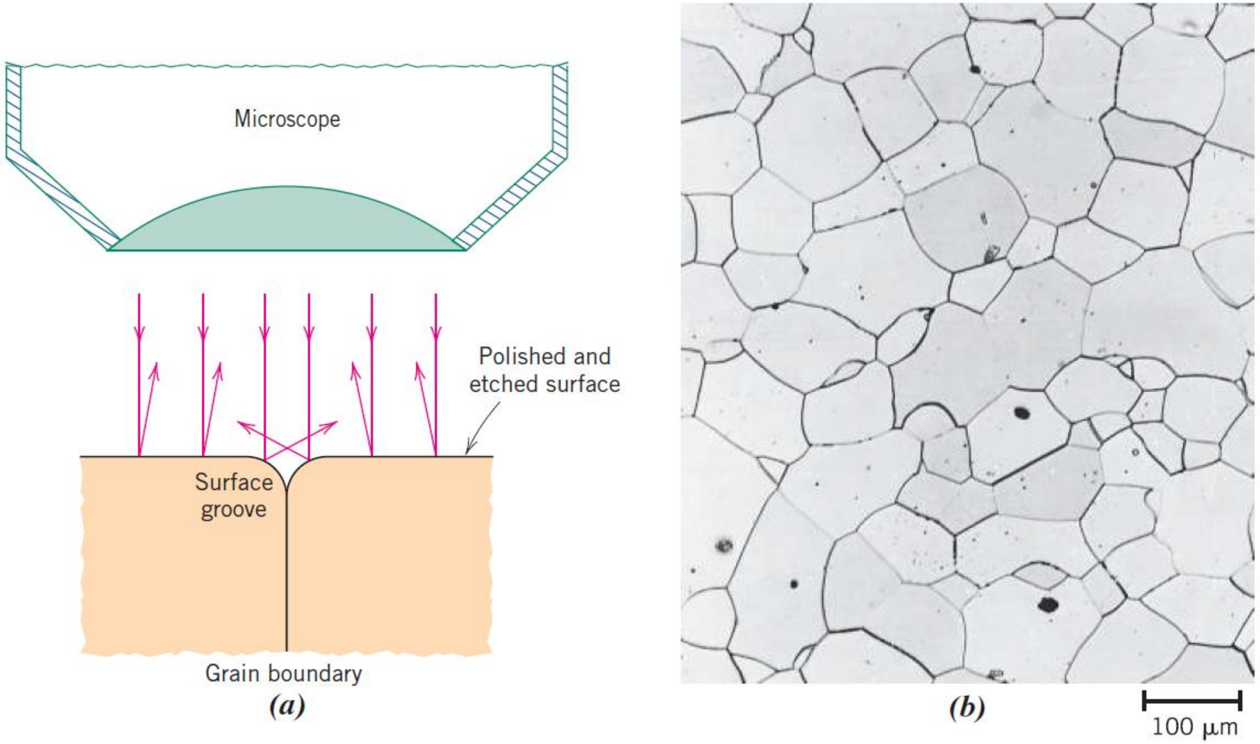
$$M = \frac{\text{measured scale length (converted to microns)}}{\text{the number appearing by the scale bar (in microns)}}$$

GRAIN-SIZE DETERMINATION

the measured scale length is approximately 10 mm, which is equivalent to (10 mm)(1000 μm/mm) = 10,000 μm. Thus, as the scale bar length is 100 μm, the magnification is equal to:

$$M = \frac{10{,}000\ \mu\text{m}}{100\ \mu\text{m}} = 100\times$$

This is the value given in the figure legend.



(*a*) Section of a grain boundary and its surface groove produced by etching; the light reflection characteristics in the vicinity of the groove are also shown.
(*b*) Photomicrograph of the surface of a polished and etched polycrystalline specimen of an iron–chromium alloy in which the grain boundaries appear dark, 100×.

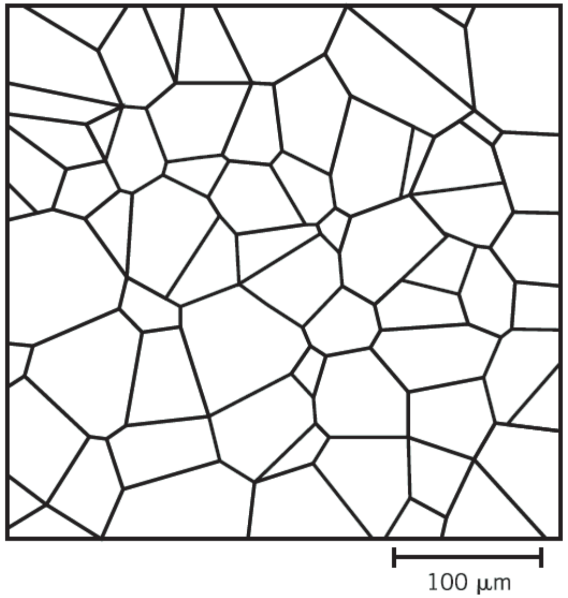
GRAIN-SIZE DETERMINATION

EXAMPLE

Grain-Size Computations Using ASTM and Intercept Methods

The following is a schematic micrograph that represents the microstructure of some hypothetical metal. Determine the following:

(a) Mean intercept length
(b) ASTM grain-size number



Solution

(a) We first determine the magnification of the micrograph. The scale bar length is measured and found to be 16 mm, which is equal to 16,000 µm; and because the scale bar number is 100 µm, the magnification is

$$M = \frac{16{,}000\ \mu\text{m}}{100\ \mu\text{m}} = 160\times$$

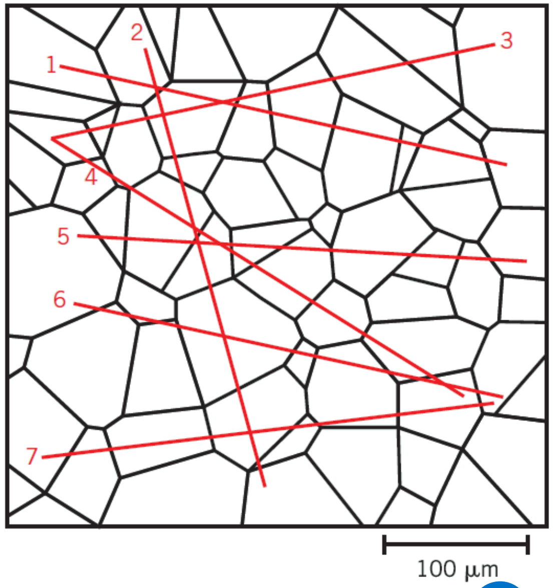
The following sketch is the same micrograph on which have been drawn seven straight lines (in red), which have been numbered.

The length of each line is 50 mm, and thus the total line length (L_T) is

$$(7\ \text{lines})(50\ \text{mm/line}) = 350\ \text{mm}$$

Tabulated next is the number of grain-boundary intersections for each line:

Line Number	*Number of Grain-Boundary Intersections*
1	8
2	8
3	8
4	9
5	9
6	9
7	7
Total	58



Thus, inasmuch as $L_T = 350$ mm, $P = 58$ grain-boundary intersections, and the magnification $M = 160\times$, the mean intercept length $\bar{\ell}$ (in millimeters in real space),

$$\bar{\ell} = \frac{L_T}{PM} = \frac{350\ \text{mm}}{(58\ \text{grain boundary intersections})(160\times)} = 0.0377\ \text{mm}$$

(b)
$$\begin{aligned} G &= -6.6457 \log \bar{\ell} - 3.298 \\ &= (-6.6457) \log(0.0377) - 3.298 \\ &= 6.16 \end{aligned}$$