

### References:

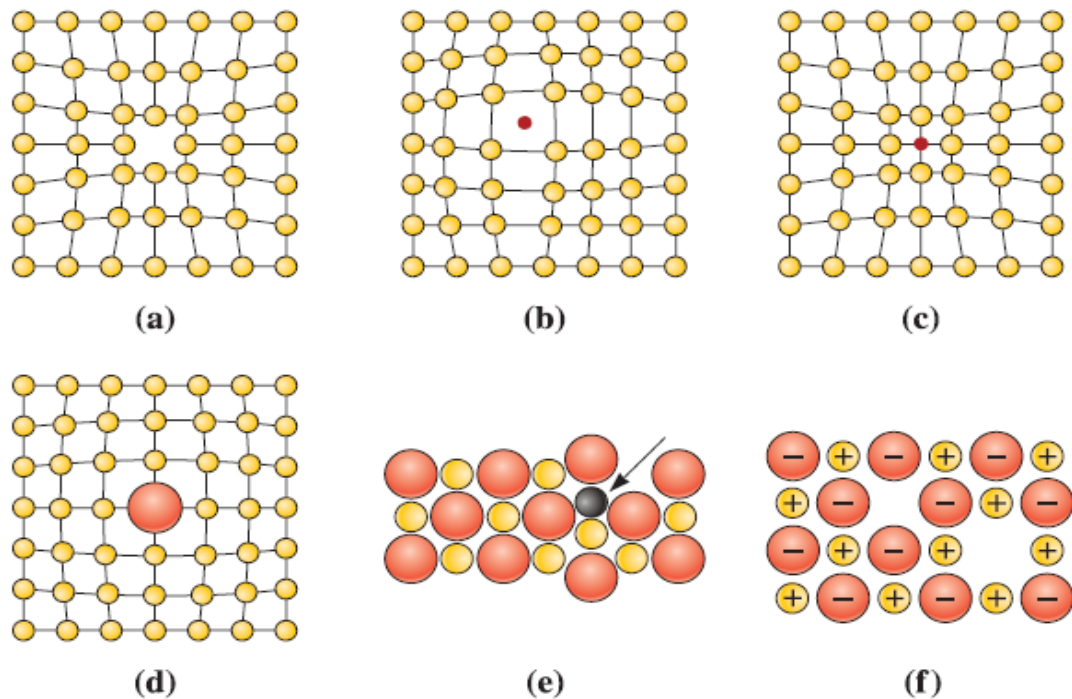
1. *Materials science and engineering an introduction, William D. Callister. Seventh edition, 2007.*
  2. *The science and engineering of materials, Donald R. Askeland, Pradeep P. Fulay and Wendelin J. Wright. Sixth Edition, 2010.*
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### *Imperfections in the atomic and ionic arrangement*

#### **1-1- Point defects**

**Point defects** are localized disruptions in otherwise perfect atomic or ionic arrangements in a crystal structure. Even though we call them point defects, the disruption affects a region involving several atoms or ions. These imperfections, shown in Figure 1-1, may be introduced by movement of the atoms or ions when they gain energy by heating, during processing of the material, or by the intentional or unintentional introduction of impurities.

Typically, **impurities** are elements or compounds that are present from raw materials or processing. For example, silicon crystals grown in quartz crucibles contain oxygen as an impurity. **Dopants**, on the other hand, are elements or compounds that are deliberately added, in known concentrations, at specific locations in the microstructure, with an intended beneficial effect on properties or processing. In general, the effect of impurities is deleterious, whereas the effect of dopants on the properties of materials is useful. Phosphorus (P) and boron (B) are examples of dopants that are added to silicon crystals to improve the electrical properties of pure silicon (Si).



**Figure 1-1 Point defects: (a) vacancy, (b) interstitial atom, (c) small substitutional atom, (d) large substitutional atom, (e) Frenkel defect, and (f) Schottky defect. All of these defects disrupt the perfect arrangement of the surrounding atoms.**

A point defect typically involves one atom or ion, or a pair of atoms or ions, and thus is different from **extended defects**, such as dislocations or grain boundaries. An important “point” about point defects is that although the defect occurs at one or two sites, their presence is “felt” over much larger distances in the crystalline material.

#### - *Vacancies*

A **vacancy** is produced when an atom or an ion is missing from its normal site in the crystal structure as in Figure 1-1(a). When atoms or ions are missing (i.e., when vacancies are present), the overall randomness or entropy of the material increases, which increases the thermodynamic stability of a crystalline material. All crystalline materials

have vacancy defects. Vacancies are introduced into metals and alloys during solidification, at high temperatures, or as a consequence of radiation damage. Vacancies play an important role in determining the rate at which atoms or ions move around or diffuse in a solid material, especially in pure metals. We will see this in greater detail in Chapter 2.

At room temperature (~298 K), the concentration of vacancies is small, but the concentration of vacancies increases exponentially as the temperature increases, as shown by the following Arrhenius type behavior:

$$n_v = n \exp\left(\frac{-Q_v}{RT}\right) \quad \dots \dots \dots (1)$$

Where

$n_v$  is the number of vacancies per  $\text{cm}^3$ ;

$n$  is the number of atoms per  $\text{cm}^3$ ;

$Q_v$  is the energy required to produce one mole of vacancies, in cal/mol or Joules/mol;

$R$  is the gas constant,  $1.987 \frac{\text{cal}}{\text{mol.K}}$  or  $8.314 \frac{\text{Joules}}{\text{mol.K}}$  and;

$T$  is the temperature in degrees Kelvin.

Due to the large thermal energy near the melting temperature, there may be as many as one vacancy per 1000 atoms. Note that this equation provides the equilibrium concentration of vacancies at a given temperature. It is also possible to retain the concentration of vacancies produced at a high temperature by quenching the material rapidly. Thus, in many situations, the concentration of vacancies observed at room temperature is not the equilibrium concentration predicted by Equation (1).

**Example (1): The Effect of Temperature on Vacancy Concentrations**

Calculate the concentration of vacancies in copper at room temperature (25°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. There are four atoms per unit cell; therefore, the number of copper atoms per cm<sup>3</sup> is:

$$n = \frac{4 \text{ atoms/cell}}{(3.6151 \times 10^{-8} \text{ cm})^3} = 8.466 \times 10^{22} \text{ copper atoms/cm}^3$$

At room temperature,  $T = 25 + 273 = 298 \text{ K}$ :

$$\begin{aligned} n_v &= n \exp\left(\frac{-Q_v}{RT}\right) \\ &= \left(8.466 \times 10^{22} \frac{\text{atoms}}{\text{cm}^3}\right) \exp\left[\frac{-20,000 \frac{\text{cal}}{\text{mol}}}{\left(1.987 \frac{\text{cal}}{\text{mol} \cdot \text{K}}\right)(298 \text{ K})}\right] \\ &= 1.814 \times 10^8 \text{ vacancies/cm}^3 \end{aligned}$$

We wish to find a heat treatment temperature that will lead to a concentration of vacancies that is 1000 times higher than this number, or  $n_v = 1.814 \times 10^{11} \text{ vacancies/cm}^3$ .

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

$$\begin{aligned} n_v &= 1.814 \times 10^{11} = n \exp\left(\frac{-Q_v}{RT}\right) \\ &= (8.466 \times 10^{22}) \exp(-20,000)/(1.987T) \\ \exp\left(\frac{-20,000}{1.987T}\right) &= \frac{1.814 \times 10^{11}}{8.466 \times 10^{22}} = 0.214 \times 10^{-11} \\ \frac{-20,000}{1.987T} &= \ln(0.214 \times 10^{-11}) = -26.87 \\ T &= \frac{20,000}{(1.987)(26.87)} = 375 \text{ K} = 102^\circ\text{C} \end{aligned}$$

By heating the copper slightly above 100°C, waiting until equilibrium is reached, and then rapidly cooling the copper back to room temperature, the number of vacancies trapped in the structure may be one thousand times greater than the equilibrium number of vacancies at room temperature. Thus, vacancy concentrations encountered in materials are often dictated by both thermodynamic and kinetic factors.

**Example (2): Vacancy Concentrations in Iron**

Calculate the theoretical density of iron, and then determine the number of vacancies needed for a BCC iron crystal to have a density of 7.874 g/cm<sup>3</sup>. The lattice parameter of iron is 2.866 x 10<sup>-8</sup> cm, and atomic weight for iron is 55.847 g/mol.

**Solution:**

The theoretical density of iron can be calculated from the lattice parameter and the atomic mass. Since the iron is BCC, two iron atoms are present in each unit cell.

$$\rho = \frac{(2 \text{ atoms/cell})(55.847 \text{ g/mol})}{(2.866 \times 10^{-8} \text{ cm})^3(6.022 \times 10^{23} \text{ atoms/mol})} = 7.879 \text{ g/cm}^3$$

This calculation assumes that there are no imperfections in the crystal. Let's calculate the number of iron atoms and vacancies that would be present in each unit cell for a density of 7.874 g/cm<sup>3</sup>:

$$\rho = \frac{(X \text{ atoms/cell})(55.847 \text{ g/mol})}{(2.866 \times 10^{-8} \text{ cm})^3(6.022 \times 10^{23} \text{ atoms/mol})} = 7.874 \text{ g/cm}^3$$

$$X \text{ atoms/cell} = \frac{(7.874 \text{ g/cm}^3)(2.866 \times 10^{-8} \text{ cm})^3(6.022 \times 10^{23} \text{ atoms/mol})}{(55.847 \text{ g/mol})} = 1.99878$$

There should be 2.00 – 1.99878 = 0.00122 vacancies per unit cell. The number of vacancies per cm<sup>3</sup> is

$$\text{Vacancies/cm}^3 = \frac{0.00122 \text{ vacancies/cell}}{(2.866 \times 10^{-8} \text{ cm})^3} = 5.18 \times 10^{19}$$


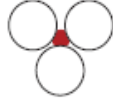
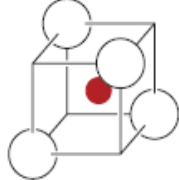

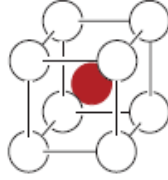
Note that other defects such as grain boundaries in a polycrystalline material contribute to a density lower than the theoretical value.

- **Interstitial Defects**

An **interstitial defect** is formed when an extra atom or ion is inserted into the crystal structure at a normally unoccupied position, as in Figure

1(b). The interstitial sites were illustrated in Table 1-1. Interstitial atoms or ions, although much smaller than the atoms or ions located at the lattice points, are still larger than the interstitial sites that they occupy; consequently, the surrounding crystal region is compressed and distorted. Interstitial atoms such as hydrogen are often present as impurities, whereas carbon atoms are intentionally added to iron to produce steel. For small concentrations, carbon atoms occupy interstitial sites in the iron crystal structure, introducing a stress in the localized region of the crystal in their vicinity. As we will see, the introduction of interstitial atoms is one important way of increasing the strength of metallic materials. Unlike vacancies, once introduced, the number of interstitial atoms or ions in the structure remains nearly constant, even when the temperature is changed.

**TABLE 1-1 The coordination number and the radius ratio**

Coordination Number	Location of Interstitial	Radius Ratio	Representation
2	Linear	0–0.155	
3	Center of triangle	0.155–0.225	
4	Center of tetrahedron	0.225–0.414	
6	Center of octahedron	0.414–0.732	
8	Center of cube	0.732–1.000	

**Example 3: Sites for Carbon in Iron**

In FCC iron, carbon atoms are located at *octahedral* sites, which occur at the center of each edge of the unit cell at sites such as (0, 0, 1/ 2) and at the center of the unit cell (1/ 2, 1/ 2, 1/ 2). In BCC iron, carbon atoms enter *tetrahedral* sites, such as (0, 1/ 2, 1/ 4). 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. (a) Would we expect a greater distortion of the crystal by an interstitial carbon atom in FCC or BCC iron? (b) What would be the atomic percentage of carbon in each type of iron if all the interstitial sites were filled?

**Solution:**

**(a)-** We can calculate the size of the interstitial site in BCC iron at the (0, 1/ 2, 1/ 4) location with the help of Figure 2(a). The radius  $R_{\text{BCC}}$  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

$$\begin{aligned} \left(\frac{1}{2} a_0\right)^2 + \left(\frac{1}{4} a_0\right)^2 &= (r_{\text{interstitial}} + R_{\text{BCC}})^2 \\ (r_{\text{interstitial}} + R_{\text{BCC}})^2 &= 0.3125a_0^2 = (0.3125)(0.2866 \text{ nm})^2 = 0.02567 \\ r_{\text{interstitial}} &= \sqrt{0.02567} - 0.1241 = 0.0361 \text{ nm} \end{aligned}$$

For FCC iron, the interstitial site such as the (0, 0, 1/ 2) lies along <001> directions. Thus, the radius of the iron atom and the radius of the interstitial site are [Figure 2(b)]:

$$\begin{aligned} R_{\text{FCC}} &= \frac{\sqrt{2}a_0}{4} = \frac{(\sqrt{2})(0.3571)}{4} = 0.1263 \text{ nm} \\ 2r_{\text{interstitial}} + 2R_{\text{FCC}} &= a_0 \\ r_{\text{interstitial}} &= \frac{0.3571 - (2)(0.1263)}{2} = 0.0523 \text{ nm} \end{aligned}$$

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

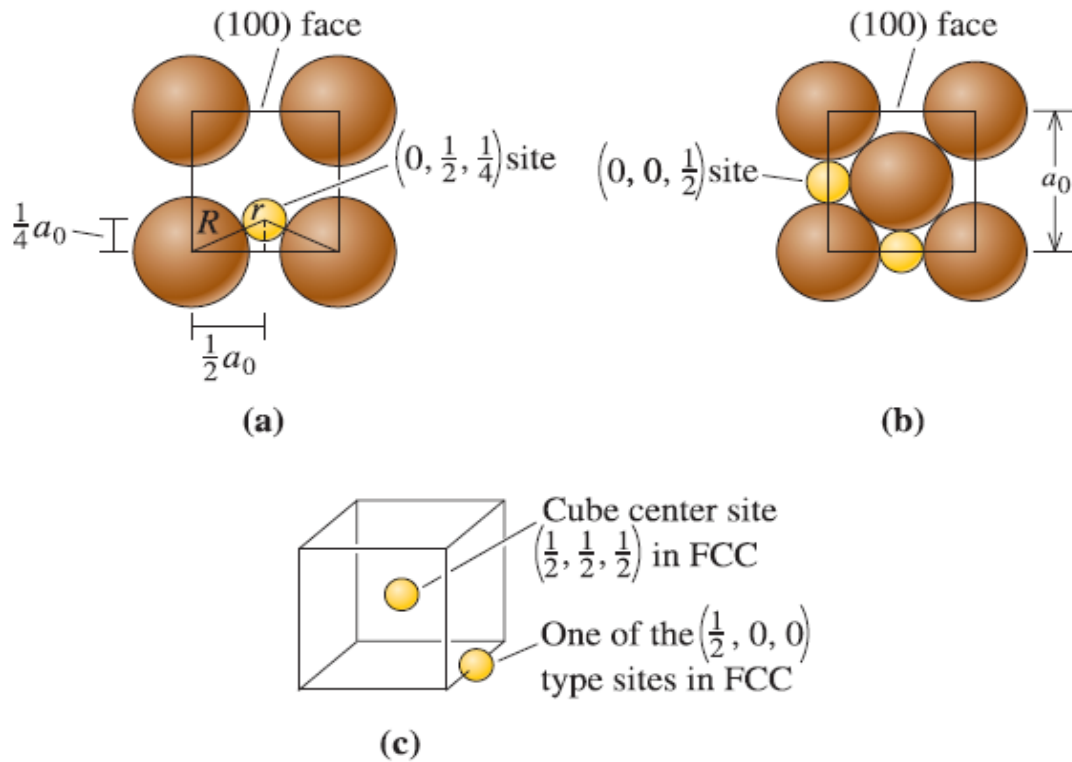


Figure 2 (a) The location of the  $(0, 1/2, 1/4)$  interstitial site in BCC metals. (b)  $(0, 0, 1/2)$  site in FCC metals. (c) Edge centers and cube centers are some of the interstitial sites in the FCC structure. (For Example 3).

**(b)-** In BCC iron, two iron atoms are expected in each unit cell. 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, there are:



$$(24 \text{ sites})\left(\frac{1}{2}\right) = 12 \text{ interstitial sites per unit cell}$$

If all of the interstitial sites were filled, the atomic percentage of carbon contained in the 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, four iron atoms are expected in each unit cell, and the number of octahedral interstitial sites is

$$(12 \text{ edges})\left(\frac{1}{4}\right) + 1 \text{ center} = 4 \text{ interstitial sites per unit cell [Figure 4 - 2(c)]}$$

Again, if all the octahedral interstitial sites were filled, the atomic percentage of carbon in the FCC iron would be

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

#### - *Substitutional Defects*

A **substitutional defect** is introduced when one atom or ion is replaced by a different type of atom or ion as in Figure 1(c) and (d). The substitutional atoms or ions occupy the normal lattice site. Substitutional atoms or ions may either be larger than the normal atoms or ions in the crystal structure, in which case the surrounding interatomic spacings are reduced, or smaller causing the surrounding atoms to have larger interatomic spacings. In either case, the substitutional defects disturb the surrounding crystal. Again, the substitutional defect can be introduced either as an impurity or as a deliberate alloying addition, and, once introduced, the number of defects is relatively independent of temperature.

Examples of substitutional defects include incorporation of dopants such as phosphorus (P) or boron (B) into Si. Similarly, if we add copper to nickel, copper atoms will occupy crystallographic sites where nickel

atoms would normally be present. The substitutional atoms will often increase the strength of the metallic material. Substitutional defects also appear in ceramic materials. For example, if we add MgO to NiO,  $\text{Mg}^{+2}$  ions occupy  $\text{Ni}^{+2}$  sites, and  $\text{O}^{-2}$  ions from MgO occupy  $\text{O}^{-2}$  sites of NiO. Whether atoms or ions go into interstitial or substitutional sites depends upon the size and valence of these guest atoms or ions compared to the size and valence of the host ions.

### 1-2- Other point defects

An **interstitialcy** is created when an atom identical to those at the normal lattice points is located in an interstitial position. These defects are most likely to be found in crystal structures having a low packing factor.

A **Frenkel defect** is a vacancy-interstitial pair formed when an ion jumps from a normal lattice point to an interstitial site, as in Figure 1(e) leaving behind a vacancy. Although, this is usually associated with ionic materials, a Frenkel defect can occur in metals and covalently bonded materials.

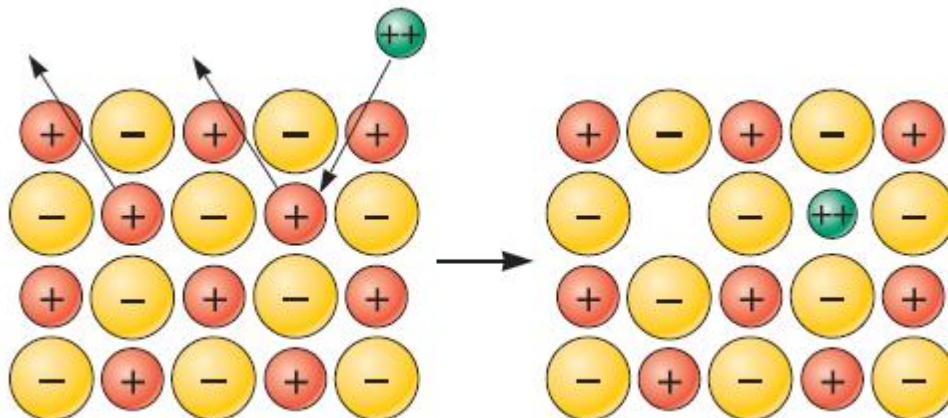
A **Schottky defect**, Figure 1(f), is unique to ionic materials and is commonly found in many ceramic materials. When vacancies occur in an ionically bonded material, a stoichiometric number of anions and cations must be missing from regular atomic positions if electrical neutrality is to be preserved. For example, one  $\text{Mg}^{+2}$  vacancy and one  $\text{O}^{-2}$  vacancy in MgO constitute a Schottky pair. In  $\text{ZrO}_2$ , for one  $\text{Zr}^{+4}$  vacancies, there will be two  $\text{O}^{-2}$  vacancies.

An important substitutional point defect occurs when an ion of one charge replaces an ion of a different charge. This might be the case when

an ion with a valence of +2 replaces an ion with a valence of +1 (Figure 3). In this case, an extra positive charge is introduced into the structure. To maintain a charge balance, a vacancy might be created where a +1 cation normally would be located. Again, this imperfection is observed in materials that have pronounced ionic bonding.

Thus, in ionic solids, when point defects are introduced, the following rules have to be observed:

- A charge balance must be maintained so that the crystalline material as a whole is electrically neutral;
- A mass balance must be maintained; and
- The number of crystallographic sites must be conserved.



**Figure 3** When a divalent cation replaces a monovalent cation, a second monovalent cation must also be removed, creating a vacancy.

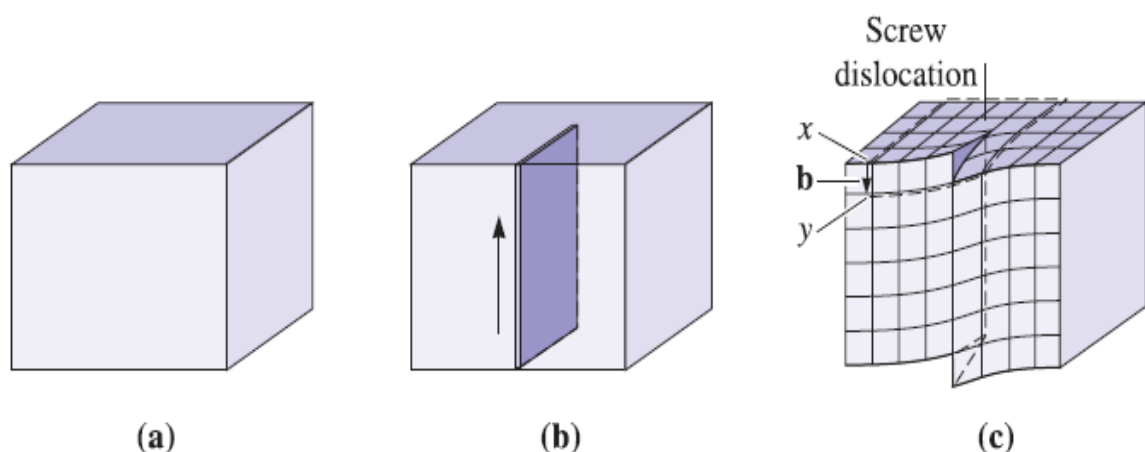
### 1-3- Dislocations

**Dislocations** are line imperfections in an otherwise perfect crystal. They typically are introduced into a crystal during solidification of the material or when the material is deformed permanently. Although dislocations are present in all materials, including ceramics and polymers,

they are particularly useful in explaining deformation and strengthening in metallic materials. We can identify three types of dislocations: the screw dislocation, the edge dislocation, and the mixed dislocation.

#### - Screw Dislocations

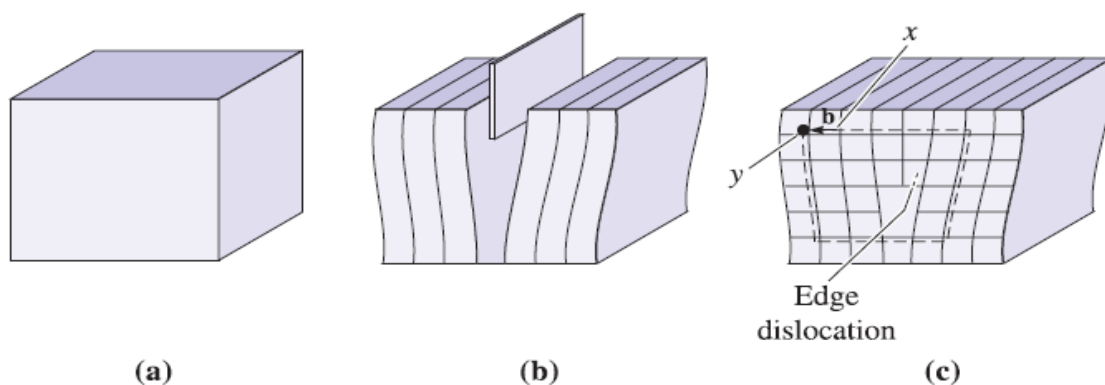
The **screw dislocation** (Figure 4) can be illustrated by cutting partway through a perfect crystal and then skewing the crystal by one atom spacing. If we follow a crystallographic plane one revolution around the axis on which the crystal was skewed, starting at point  $x$  and traveling equal atom spacings in each direction, we finish at point  $y$  one atom spacing below our starting point. If a screw dislocation were not present, the loop would close. The vector required to complete the loop is the **Burgers vector  $b$** . If we continued our rotation, we would trace out a spiral path. The axis or line around which we trace out this path, is the screw dislocation. The Burgers vector is parallel to the screw dislocation.



**Figure 4** The perfect crystal (a) is cut and sheared one atom spacing, (b) and (c). The line along which shearing occurs is a screw dislocation. A Burgers vector  $b$  is required to close a loop of equal atom spacings around the screw dislocation.

- *Edge Dislocations*

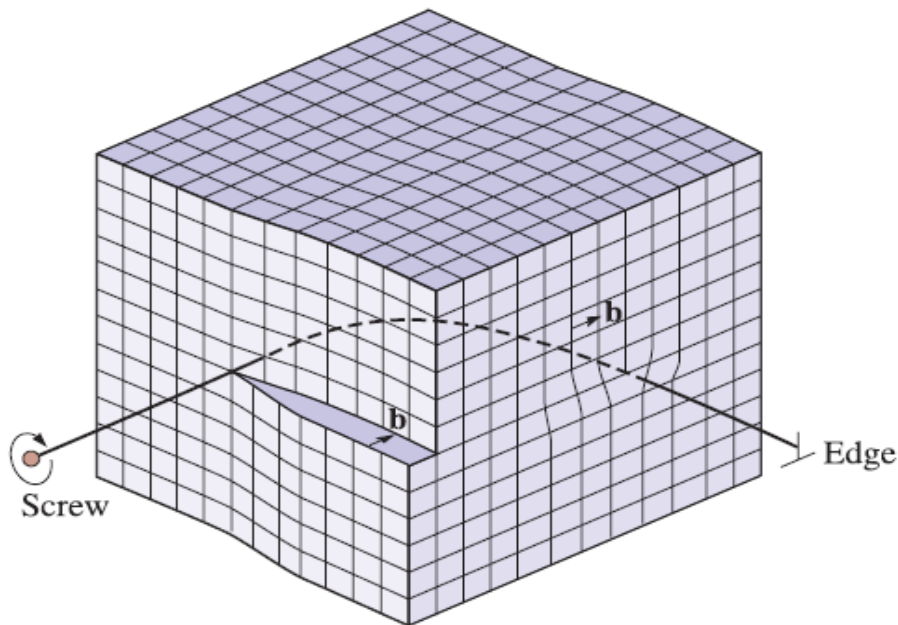
An **edge dislocation** (Figure 5) can be illustrated by slicing partway through a perfect crystal, spreading the crystal apart, and partly filling the cut with an extra half plane of atoms. The bottom edge of this inserted plane represents the edge dislocation. If we describe a clockwise loop around the edge dislocation, starting at point  $x$  and traveling an equal number of atom spacings in each direction, we finish at point  $y$  one atom spacing from the starting point. If an edge dislocation were not present, the loop would close. The vector required to complete the loop is, again, the Burgers vector. In this case, the Burgers vector is perpendicular to the dislocation. By introducing the dislocation, the atoms above the dislocation line are squeezed too closely together, while the atoms below the dislocation are stretched too far apart. The surrounding region of the crystal has been disturbed by the presence of the dislocation. A “ $\perp$ ” symbol is often used to denote an edge dislocation. The long axis of the “ $\perp$ ” points toward the extra half plane. Unlike an edge dislocation, a screw dislocation cannot be visualized as an extra half plane of atoms.



**Figure 4-5** The perfect crystal in (a) is cut and an extra half plane of atoms is inserted (b). The bottom edge of the extra half plane is an edge dislocation (c). A Burgers vector  $\mathbf{b}$  is required to close a loop of equal atom spacings around the edge dislocation.

- *Mixed Dislocations*

As shown in (Figure 6), **mixed dislocations** have both edge and screw components, with a transition region between them. The Burgers vector, however, remains the same for all portions of the mixed dislocation.



**Figure 6** 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.

**1-4- 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. At any instant of time not all atoms vibrate at the same frequency and amplitude, nor with the same energy. At a given temperature there will exist a distribution of energies for the constituent atoms about an average energy.

Over time the vibrational energy of any specific atom will also vary 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.