

Elementary Materials Science Concepts¹

Understanding the basic building blocks of matter has been one of the most intriguing endeavors of humankind. Our understanding of interatomic interactions has now reached a point where we can quite comfortably explain the macroscopic properties of matter, based on quantum mechanics and electrostatic interactions between electrons and ionic nuclei in the material. There are many properties of materials that can be explained by a classical treatment of the subject. In this chapter, as well as Chapter 2, we treat the interactions in a material from a classical perspective and introduce a number of elementary concepts. These concepts do not invoke any quantum mechanics, which is a subject of modern physics and is introduced in Chapter 3. Although many useful engineering properties of materials can be treated with hardly any quantum mechanics, it is impossible to develop the science of electronic materials and devices without modern physics.

1.1 ATOMIC STRUCTURE AND ATOMIC NUMBER

The model of the atom that we must use to understand the atom's general behavior involves quantum mechanics, a topic we will study in detail in Chapter 3. For the present, we will simply accept the following facts about a simplified, but intuitively satisfactory, atomic model called the **shell model**, based on the **Bohr model** (1913).

The mass of the atom is concentrated at the nucleus, which contains protons and neutrons. Protons are positively charged particles, whereas neutrons are neutral particles, and both have about the same mass. Although there is a Coulombic repulsion between the protons, all the protons and neutrons are held together in the nucleus by the

¹ This chapter may be skipped by readers who have already been exposed to an elementary course in materials science.

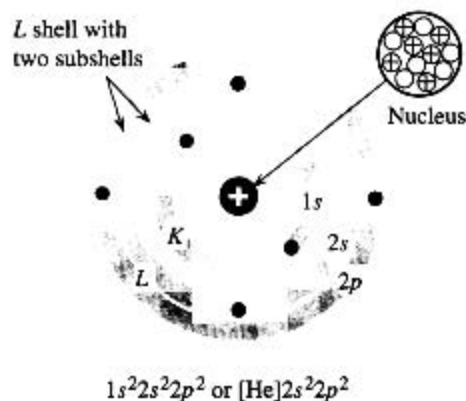


Figure 1.1 The shell model of the carbon atom, in which the electrons are confined to certain shells and subshells within shells.

strong force, which is a powerful, fundamental, natural force between particles. This force has a very short range of influence, typically less than 10^{-15} m. When the protons and neutrons are brought together very closely, the strong force overcomes the electrostatic repulsion between the protons and keeps the nucleus intact. The number of protons in the nucleus is the **atomic number Z** of the element.

The electrons are assumed to be orbiting the nucleus at very large distances compared to the size of the nucleus. There are as many orbiting electrons as there are protons in the nucleus. An important assumption in the Bohr model is that only certain orbits with fixed radii are stable around the nucleus. For example, the closest orbit of the electron in the hydrogen atom can only have a radius of 0.053 nm. Since the electron is constantly moving around an orbit with a given radius, over a long time period (perhaps $\sim 10^{-12}$ seconds on the atomic time scale), the electron would appear as a spherical negative-charge cloud around the nucleus and not as a single dot representing a finite particle. We can therefore view the electron as a charge contained within a spherical **shell** of a given radius.

Due to the requirement of stable orbits, the electrons therefore do not randomly occupy the whole region around the nucleus. Instead, they occupy various well-defined spherical regions. They are distributed in various shells and **subshells** within the shells, obeying certain occupation (or seating) rules.² The example for the carbon atom is shown in Figure 1.1.

The shells and subshells that define the whereabouts of the electrons are labeled using two sets of integers, n and ℓ . These integers are called the **principal** and **orbital angular momentum quantum numbers**, respectively. (The meanings of these names are not critical at this point.) The integers n and ℓ have the values $n = 1, 2, 3, \dots$, and $\ell = 0, 1, 2, \dots, n - 1$, and $\ell < n$. For each choice of n , there are n values of ℓ , so higher-order shells contain more subshells. The shells corresponding to $n = 1, 2, 3, 4, \dots$

² In Chapter 3, in which we discuss the quantum mechanical model of the atom, we will see that these shells and subshells are spatial regions around the nucleus where the electrons are most likely to be found.

Table 1.1 Maximum possible number of electrons in the shells and subshells of an atom

<i>n</i>	Shell	Subshell			
		$\ell = 0$	1	2	3
		<i>s</i>	<i>p</i>	<i>d</i>	<i>f</i>
1	<i>K</i>	2			
2	<i>L</i>	2	6		
3	<i>M</i>	2	6	10	
4	<i>N</i>	2	6	10	14

are labeled by the capital letters *K, L, M, N, ...*, and the subshells denoted by $\ell = 0, 1, 2, 3, \dots$ are labeled *s, p, d, f, ...*. The subshell with $\ell = 1$ in the $n = 2$ shell is thus labeled the $2p$ subshell, based on the standard notation $n\ell$.

There is a definite rule to filling up the subshells with electrons; we cannot simply put all the electrons in one subshell. The number of electrons a given subshell can take is fixed by nature to be $2(2\ell + 1)$. For the *s* subshell ($\ell = 0$), there are two electrons, whereas for the *p* subshell, there are six electrons, and so on. Table 1.1 summarizes the most number of electrons that can be put into various subshells and shells of an atom. Obviously, the larger the shell, the more electrons it can take, simply because it contains more subshells. The shells and subshells are filled starting with those closest to the nucleus as explained next.

The number of electrons in a subshell is indicated by a superscript on the subshell symbol, so the electronic structure, or configuration, of the carbon atom (atomic number 6) shown in Figure 1.1 becomes $1s^2 2s^2 2p^2$. The *K* shell has only one subshell, which is full with two electrons. This is the structure of the inert element He. We can therefore write the electronic configuration more simply as $[\text{He}]2s^2 2p^2$. The general rule is put the nearest previous inert element, in this case He, in square brackets and write the subshells thereafter.

The electrons occupying the outer subshells are the farthest away from the nucleus and have the most important role in atomic interactions, as in chemical reactions, because these electrons are the first to interact with outer electrons on neighboring atoms. The outermost electrons are called **valence electrons** and they determine the **valency** of the atom. Figure 1.1 shows that carbon has four valence electrons in the *L* shell.

When a subshell is full of electrons, it cannot accept any more electrons and it is said to have acquired a stable configuration. This is the case with the inert elements at the right-hand side of the Periodic Table, all of which have completely filled subshells and are rarely involved in chemical reactions. The majority of such elements are gases inasmuch as the atoms do not bond together easily to form a

³ We will actually show this in Chapter 3 using quantum mechanics.

liquid or solid. They are sometimes used to provide an inert atmosphere instead of air for certain reactive materials.

In an atom such as the Li atom, there are two electrons in the $1s$ subshell and one electron in the $2s$ subshell. The atomic structure of Li is $1s^2 2s^1$. The third electron is in the $2s$ subshell, rather than any other subshell, because this is the arrangement of the electrons that results in the lowest overall energy for the whole atom. It requires energy (work) to take the third electron from the $2s$ to the $2p$ or higher subshells as will be shown in Chapter 3. Normally the zero energy reference corresponds to the electron being at infinity, that is, isolated from the atom. When the electron is inside the atom, its energy is negative, which is due to the attraction of the positive nucleus. An electron that is closer to the nucleus has a lower energy. The electrons nearer the nucleus are more closely bound and have higher binding energies. The $1s^2 2s^1$ configuration of electrons corresponds to the lowest energy structure for Li and, at the same time, obeys the occupation rules for the subshells. If the $2s$ electron is somehow excited to another outer subshell, the energy of the atom increases, and the atom is said to be **excited**.

The smallest energy required to remove a single electron from a neutral atom and thereby create a positive ion (*cation*) and an isolated electron is defined as the **ionization energy** of the atom. The Na atom has only a single valence electron in its outer shell, which is the easiest to remove. The energy required to remove this electron is 5.1 eV, which is the Na atom's ionization energy. The **electron affinity** represents the energy that is needed, or released, when we add an electron to a neutral atom to create a negative ion (*anion*). Notice that the ionization term implies the generation of a positive ion, whereas the electron affinity implies that we have created a negative ion. Certain atoms, notably the halogens (such as F, Cl, Br, I), can actually attract an electron to form a negative ion. Their electron affinities are negative. When we place an electron into a Cl atom, we find that an energy of 3.6 eV is *released*. The Cl^- ion has a lower energy than the Cl atom, which means that it is energetically favorable to form a Cl^- ion by introducing an electron into the Cl atom.

There is a very useful theorem in physics, called the **Virial theorem**, that allows us to relate the average kinetic energy \overline{KE} , average potential energy \overline{PE} , and average total or overall energy \overline{E} of an electron in an atom, or electrons and nuclei in a molecule, through remarkably simple relationships,⁴

Virial
theorem

$$\overline{E} = \overline{KE} + \overline{PE} \quad \text{and} \quad \overline{KE} = -\frac{1}{2}\overline{PE} \quad [1.1]$$

For example, if we define zero energy for the H atom as the H^+ ion and the electron infinitely separated, then the energy of the electron in the H atom is -13.6 electron volts (eV). It takes 13.6 eV to ionize the H atom. The average \overline{PE} of the electron, due to its Coulombic interaction with the positive nucleus, is -27.4 eV. Its average \overline{KE} turns out to be 13.6 eV. Example 1.1 uses the Virial theorem to calculate the radius of the hydrogen atom, the velocity of the electron, and its frequency of rotation.

⁴ While the final result stated in Equation 1.1 is elegantly simple, the actual proof is quite involved and certainly not trivial. As stated here, the Virial theorem applies to a system of charges that interact through electrostatic forces only.

VIRIAL THEOREM AND THE BOHR ATOM Consider the hydrogen atom in Figure 1.2 in which the electron is in the stable 1s orbit with a radius r_0 . The ionization energy of the hydrogen atom is 13.6 eV.

EXAMPLE 1.1

- It takes 13.6 eV to ionize the hydrogen atom, i.e., to remove the electron to infinity. If the condition when the electron is far removed from the hydrogen nucleus defines the zero reference of energy, then the total energy of the electron within the H atom is -13.6 eV. Calculate the average PE and average KE of the electron.
- Assume that the electron is in a stable orbit of radius r_0 around the positive nucleus. What is the Coulombic PE of the electron? Hence, what is the radius r_0 of the electron orbit?
- What is the velocity of the electron?
- What is the frequency of rotation (oscillation) of the electron around the nucleus?

SOLUTION

- a. From Equation 1.1 we obtain

$$\overline{E} = \overline{PE} + \overline{KE} = \frac{1}{2}\overline{PE}$$

or
$$\overline{PE} = 2\overline{E} = 2 \times (-13.6 \text{ eV}) = -27.2 \text{ eV}$$

The average kinetic energy is

$$\overline{KE} = -\frac{1}{2}\overline{PE} = 13.6 \text{ eV}$$

- b. The Coulombic PE of interaction between two charges Q_1 and Q_2 separated by a distance r_0 , from elementary electrostatics, is given by

$$PE = \frac{Q_1 Q_2}{4\pi\epsilon_0 r_0} = \frac{(-e)(+e)}{4\pi\epsilon_0 r_0} = -\frac{e^2}{4\pi\epsilon_0 r_0}$$

where we substituted $Q_1 = -e$ (electron's charge), and $Q_2 = +e$ (charge of nucleus). Thus the radius r_0 is

$$\begin{aligned} r_0 &= -\frac{(1.6 \times 10^{-19} \text{ C})^2}{4\pi(8.85 \times 10^{-12} \text{ F m}^{-1})(-27.2 \text{ eV} \times 1.6 \times 10^{-19} \text{ J/eV})} \\ &= 5.29 \times 10^{-11} \text{ m} \quad \text{or} \quad 0.0529 \text{ nm} \end{aligned}$$

which is called the **Bohr radius** (also denoted a_0).

Stable orbit has radius r_0

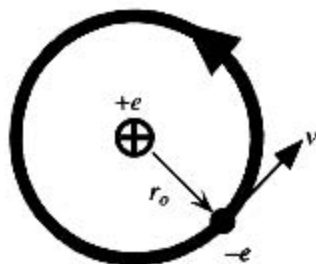


Figure 1.2 The planetary model of the hydrogen atom in which the negatively charged electron orbits the positively charged nucleus.

c. Since $KE = \frac{1}{2}m_e v^2$, the average velocity is

$$v = \sqrt{\frac{KE}{\frac{1}{2}m_e}} = \sqrt{\frac{13.6 \text{ eV} \times 1.6 \times 10^{-19} \text{ J/eV}}{\frac{1}{2}(9.1 \times 10^{-31} \text{ kg})}} = 2.19 \times 10^6 \text{ m s}^{-1}$$

d. The period of orbital rotation T is

$$T = \frac{2\pi r_o}{v} = \frac{2\pi(0.0529 \times 10^{-9} \text{ m})}{2.19 \times 10^6 \text{ m s}^{-1}} = 1.52 \times 10^{-16} \text{ seconds}$$

The orbital frequency $\nu = 1/T = 6.59 \times 10^{15} \text{ s}^{-1}$ (Hz).

1.2 ATOMIC MASS AND MOLE

We had defined the atomic number Z as the number of protons in the nucleus of an atom. The **atomic mass number** A is simply the total number of protons and neutrons in the nucleus. It may be thought that we can use the atomic mass number A of an atom to gauge its atomic mass, but this is done slightly differently to account for the existence of different isotopes of an element; isotopes are atoms of a given element that have the same number of protons but a different number of neutrons in the nucleus. The **atomic mass unit** (amu) u is a convenient atomic mass unit that is equal to $\frac{1}{12}$ of the mass of a neutral carbon atom which has a mass number $A = 12$ (6 protons and 6 neutrons). It has been found that $u = 1.66054 \times 10^{-27} \text{ kg}$.

The **atomic mass** or **relative atomic mass** or simply **atomic weight** M_{at} of an element is the average atomic mass, in atomic mass units, of all the naturally occurring isotopes of the element. Atomic masses are listed in the Periodic Table. **Avogadro's number** N_A is the number of atoms in exactly 12 grams of carbon-12, which is 6.022×10^{23} to three decimal places. Since the atomic mass M_{at} is defined as $\frac{1}{12}$ of the mass of the carbon-12 atom, it is straightforward to show that N_A number of atoms of any substance has a mass equal to the atomic mass M_{at} in grams.

A **mole** of a substance is that amount of the substance which contains exactly Avogadro's number N_A of atoms or molecules that make up the substance. One mole of a substance has a mass as much as its atomic (molecular) mass in grams. For example, 1 mole of copper contains 6.022×10^{23} number of copper atoms and has a mass of 63.55 grams. Thus, an amount of an element which has 6.022×10^{23} atoms has a mass in grams equal to the atomic mass. This means we can express the atomic mass as grams per unit mole (g mol^{-1}). The atomic mass of Au is 196.97 amu or g mol^{-1} . Thus, a 10 gram bar of gold has $(10 \text{ g}) / (196.97 \text{ g mol}^{-1})$ or 0.0507 moles.

Frequently we have to convert the composition of a substance from atomic percentage to weight percentage, and vice versa. Compositions in materials engineering generally use weight percentages, whereas chemical formulas are given in terms of atomic composition. Suppose that a substance (an alloy or a compound) is composed of two elements, A and B. Let the *weight fractions* of A and B be w_A and w_B , respectively. Let n_A and n_B be the *atomic* or *molar fractions* of A and B; that is, n_A represents the fraction of type A atoms, n_B represents the fraction of type B atoms in the whole

substance, and $n_A + n_B = 1$. Suppose that the atomic masses of A and B are M_A and M_B . Then n_A and n_B are given by

$$n_A = \frac{w_A/M_A}{w_A/M_A + w_B/M_B} \quad \text{and} \quad n_B = 1 - n_A \quad [1.2]$$

*Weight to
atomic
percentage*

where $w_A + w_B = 1$. Equation 1.2 can be readily rearranged to obtain w_A and w_B in terms of n_A and n_B .

COMPOSITIONS IN ATOMIC AND WEIGHT PERCENTAGES Consider a Pb–Sn solder that is 38.1 wt.% Pb and 61.9 wt.% Sn (this is the eutectic composition with the lowest melting point). What are the atomic fractions of Pb and Sn in this solder?

EXAMPLE 1.2

SOLUTION

For Pb, the weight fraction and atomic mass are respectively $w_A = 0.381$ and $M_A = 207.2 \text{ g mol}^{-1}$ and for Sn, $w_B = 0.619$ and $M_B = 118.71 \text{ g mol}^{-1}$. Thus, Equation 1.2 gives

$$n_A = \frac{w_A/M_A}{w_A/M_A + w_B/M_B} = \frac{(0.381)/(207.2)}{0.381/207.2 + 0.619/118.71} = 0.261 \quad \text{or} \quad 26.1 \text{ at.}\%$$

and

$$n_B = \frac{w_B/M_B}{w_A/M_A + w_B/M_B} = \frac{(0.619)/(118.71)}{0.381/207.2 + 0.619/118.71} = 0.739 \quad \text{or} \quad 73.9 \text{ at.}\%$$

Thus the alloy is 26.1 at.% Pb and 73.9 at.% Sn which can be written as $\text{Pb}_{0.261}\text{Sn}_{0.739}$.

1.3 BONDING AND TYPES OF SOLIDS

1.3.1 MOLECULES AND GENERAL BONDING PRINCIPLES

When two atoms are brought together, the valence electrons interact with each other and with the neighbor's positively charged nucleus. The result of this interaction is often the formation of a bond between the two atoms, producing a molecule. The formation of a bond means that the energy of the system of two atoms together must be less than that of the two atoms separated, so that the molecule formation is energetically favorable, that is, more stable. The general principle of molecule formation is illustrated in Figure 1.3a, showing two atoms brought together from infinity. As the two atoms approach each other, the atoms exert attractive and repulsive forces on each other as a result of mutual electrostatic interactions. Initially, the attractive force F_A dominates over the repulsive force F_R . The net force F_N is the sum of the two,

$$F_N = F_A + F_R$$

Net force

and this is initially attractive, as indicated in Figure 1.3a.

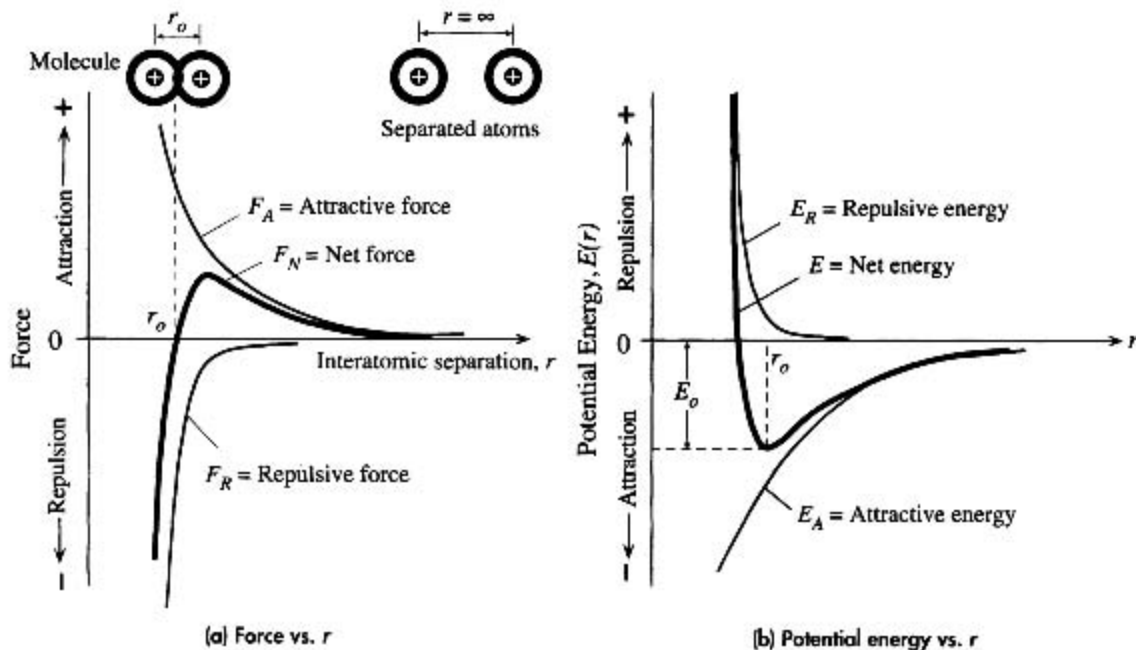


Figure 1.3 (a) Force versus interatomic separation and (b) potential energy versus interatomic separation.

The potential energy $E(r)$ of the two atoms can be found from⁵

Net force and
potential
energy

$$F_N = \frac{dE}{dr}$$

by integrating the net force F_N . Figure 1.3a and b shows the variation of the net force $F_N(r)$ and the overall potential energy $E(r)$ with the interatomic separation r as the two atoms are brought together from infinity. The lowering of energy corresponds to an attractive interaction between the two atoms.

Net force in
bonding
between
atoms

The variations of F_A and F_R with distance are different. Force F_A varies slowly, whereas F_R varies strongly with separation and is strongest when the two atoms are very close. When the atoms are so close that the individual electron shells overlap, there is a very strong electron-to-electron shell repulsion and F_R dominates. An equilibrium will be reached when the attractive force just balances the repulsive force and the net force is zero, or

$$F_N = F_A + F_R = 0 \quad [1.3]$$

In this state of equilibrium, the atoms are separated by a certain distance r_o , as shown in Figure 1.3. This distance is called the equilibrium separation and is effectively the **bond length**. On the energy diagram, $F_N = 0$ means $dE/dr = 0$, which means that the equilibrium of two atoms corresponds to the potential energy of the

⁵ Remember that the change dE in the PE is the work done against the force, $dE = F_N dr$.

system acquiring its minimum value. Consequently, the molecule will only be formed if the energy of the two atoms as they approach each other can attain a minimum. This minimum energy also defines the bond energy of the molecule, as depicted in Figure 1.3b. An energy of E_o is required to separate the two atoms, and this represents the **bond energy**.

Although we considered only two atoms, similar arguments also apply to bonding between many atoms, or between millions of atoms as in a typical solid. Although the actual details of F_A and F_R will change from material to material, the general principle that there is a bonding energy E_o per atom and an equilibrium interatomic separation r_o will still be valid. Even in a solid in the presence of many interacting atoms, we can still identify a general potential energy curve $E(r)$ per atom similar to the type shown in Figure 1.3b. We can also use the curve to understand the properties of the solid, such as the thermal expansion coefficient and elastic and bulk moduli.

1.3.2 COVALENTLY BONDED SOLIDS: DIAMOND

Two atoms can form a bond with each other by sharing some or all of their valence electrons and thereby reducing the overall potential energy of the combination. The covalent bond results from the sharing of valence electrons to complete the subshells of each atom. Figure 1.4 shows the formation of a covalent bond between two hydrogen atoms as they come together to form the H_2 molecule. When the $1s$ subshells overlap, the electrons are shared by both atoms and each atom now has a complete subshell. As illustrated in Figure 1.4, electrons 1 and 2 must now orbit both atoms; they therefore cross the overlap region more frequently, indeed twice as often. Thus, electron sharing,

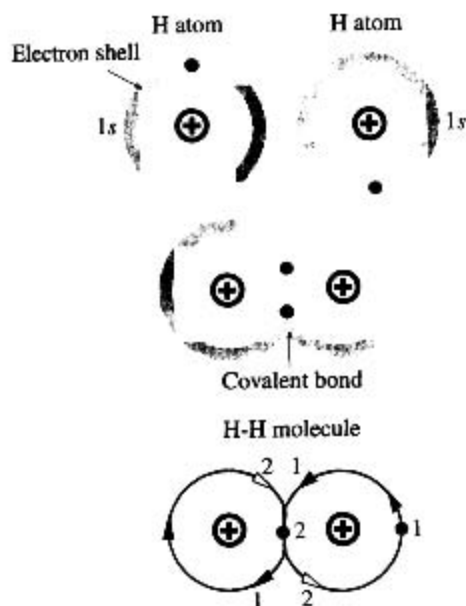


Figure 1.4 Formation of a covalent bond between two H atoms, leading to the H_2 molecule. Electrons spend a majority of their time between the two nuclei, which results in a net attraction between the electrons and the two nuclei, which is the origin of the covalent bond.

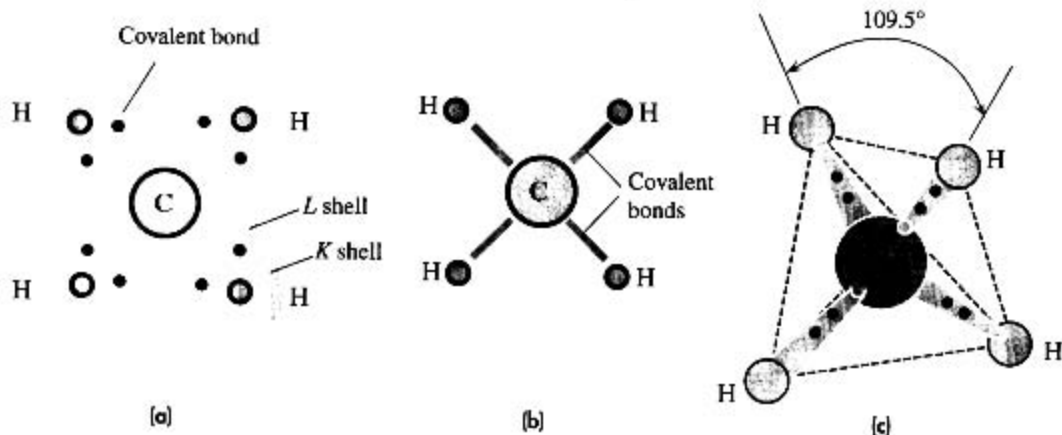


Figure 1.5

(a) Covalent bonding in methane, CH_4 , which involves four hydrogen atoms sharing electrons with one carbon atom.

Each covalent bond has two shared electrons. The four bonds are identical and repel each other.

(b) Schematic sketch of CH_4 on paper.

(c) In three dimensions, due to symmetry, the bonds are directed toward the corners of a tetrahedron.

on average, results in a greater concentration of negative charge in the region between the two nuclei, which keeps the two nuclei bonded to each other. Furthermore, by synchronizing their motions, electrons 1 and 2 can avoid crossing the overlap region at the same time. For example, when electron 1 is at the far right (or left), electron 2 is in the overlap region; later, the situation is reversed.

The electronic structure of the carbon atom is $[\text{He}]2s^22p^2$ with four empty seats in the $2p$ subshell. The $2s$ and $2p$ subshells, however, are quite close. When other atoms are in the vicinity, as a result of interatomic interactions, the two subshells become indistinguishable and we can consider only the shell itself, which is the L shell with a capacity of eight electrons. It is clear that the C atom with four vacancies in the L shell can readily share electrons with four H atoms, as depicted in Figure 1.5, whereby the C atom and each of the H atoms attain complete shells. This is the CH_4 molecule, which is the gas methane. The repulsion between the electrons in one bond and the electrons in a neighboring bond causes the bonds to spread as far out from each other as possible, so that in three dimensions, the H atoms occupy the corners of an imaginary tetrahedron and the CH bonds are at an angle of 109.5° to each other, as sketched in Figure 1.5.

The C atom can also share electrons with other C atoms, as shown in Figure 1.6. Each neighboring C atom can share electrons with other C atoms, leading to a three-dimensional network of a covalently bonded structure. This is the structure of the precious diamond crystal, in which all the carbon atoms are covalently bonded to each other, as depicted in the figure. The **coordination number (CN)** is the number of nearest neighbors for a given atom in the solid. As is apparent in Figure 1.6, the coordination number for a carbon atom in the diamond crystal structure is 4.

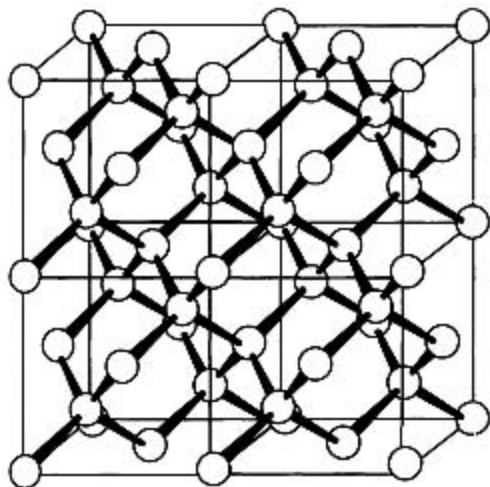


Figure 1.6 The diamond crystal is a covalently bonded network of carbon atoms. Each carbon atom is bonded covalently to four neighbors, forming a regular three-dimensional pattern of atoms that constitutes the diamond crystal.

Due to the strong Coulombic attraction between the shared electrons and the positive nuclei, the covalent bond energy is usually the highest for all bond types, leading to very high melting temperatures and very hard solids: diamond is one of the hardest known materials.

Covalently bonded solids are also insoluble in nearly all solvents. The directional nature and strength of the covalent bond also make these materials nonductile (or nonmalleable). Under a strong force, they exhibit brittle fracture. Further, since all the valence electrons are locked in the bonds between the atoms, these electrons are not free to drift in the crystal when an electric field is applied. Consequently, the electrical conductivity of such materials is very poor.

1.3.3 METALLIC BONDING: COPPER

Metal atoms have only a few valence electrons, which are not very difficult to remove. When many metal atoms are brought together to form a solid, these valence electrons are lost from individual atoms and become collectively shared by all the ions. The valence electrons therefore become **delocalized** and form an **electron gas** or **electron cloud**, permeating the space between the ions, as depicted in Figure 1.7. The attraction between the negative charge of this electron gas and the metal ions more than compensates for the energy initially required to remove the valence electrons from the individual atoms. Thus, the bonding in a metal is essentially due to the attraction between the stationary metal ions and the freely wandering electrons between the ions.

The bond is a **collective sharing** of electrons and is therefore nondirectional. Consequently, the metal ions try to get as close as possible, which leads to **close-packed crystal** structures with high coordination numbers, compared to covalently bonded solids. In the particular example shown in Figure 1.7, Cu^+ ions are packed as closely as possible by the gluing effect of the electrons between the ions, forming a crystal

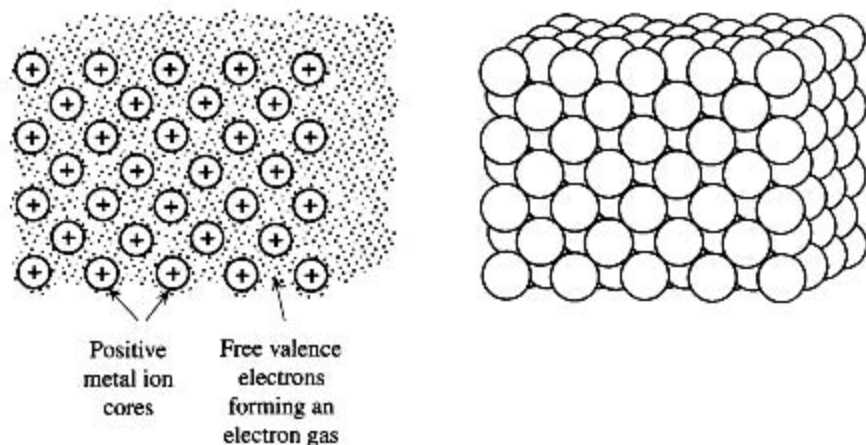


Figure 1.7 In metallic bonding, the valence electrons from the metal atoms form a “cloud of electrons,” which fills the space between the metal ions and “glues” the ions together through Coulombic attraction between the electron gas and the positive metal ions.

structure called the **face-centered cubic (FCC)**. The FCC crystal structure, as explained later in Section 1.8, has Cu^+ ions at the corners of a cube and a Cu^+ at the center of each cube-face. (See Figure 1.31.)

The results of this type of bonding are dramatic. First, the nondirectional nature of the bond means that under an applied force, metal ions are able to move with respect to each other, especially in the presence of certain crystal defects (such as dislocations). Thus, metals tend to be ductile. Most importantly, however, the “free” valence electrons in the electron gas can respond readily to an applied electric field and drift along the force of the field, which is the reason for the high electrical conductivity of metals. Furthermore, if there is a temperature gradient along a metal bar, the free electrons can also contribute to the energy transfer from the hot to the cold regions, since they frequently collide with the metal ions and thereby transfer energy. Metals therefore, typically, also have good thermal conductivities; that is, they easily conduct heat. This is why when you touch your finger to a metal it feels cold because it conducts heat “away” from the finger to the ambient (making the fingertip “feel” cold).

1.3.4 IONICALLY BONDED SOLIDS: SALT

Common table salt, NaCl , is a classic example of a solid in which the atoms are held together by ionic bonding. Ionic bonding is frequently found in materials that normally have a metal and a nonmetal as the constituent elements. Sodium (Na) is an alkaline metal with only one valence electron that can easily be removed to form an Na^+ ion with complete subshells. The ion Na^+ looks like the inert element Ne , but with a positive charge. Chlorine has five electrons in its $3p$ subshell and can readily accept

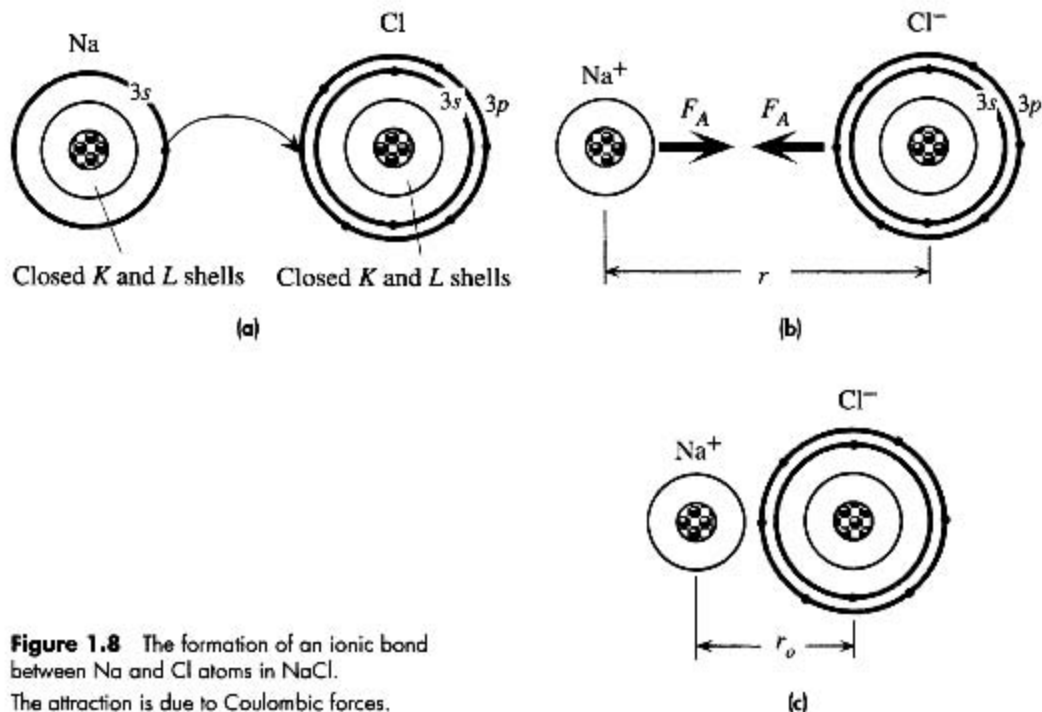


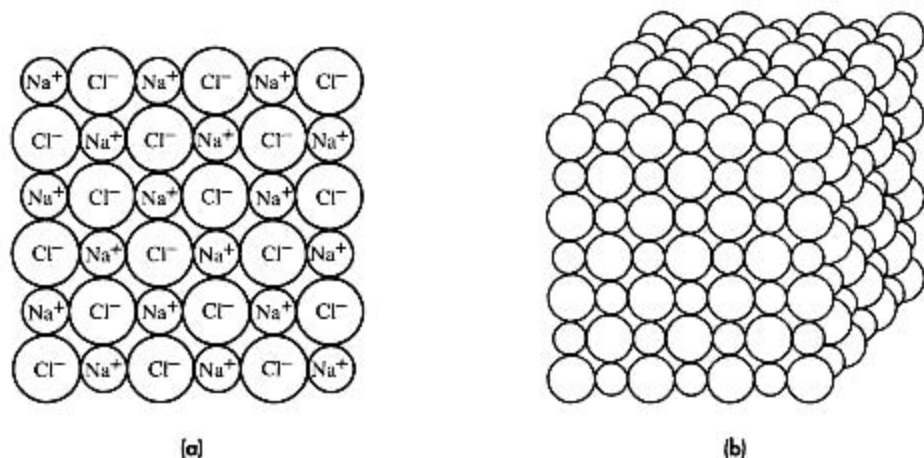
Figure 1.8 The formation of an ionic bond between Na and Cl atoms in NaCl.

The attraction is due to Coulombic forces.

one more electron to close this subshell. By taking the electron given up by the Na atom, the Cl atom becomes negatively charged and looks like the inert element Ar with a net negative charge. Transferring the valence electron of Na to Cl thus results in two oppositely charged ions, Na^+ and Cl^- , which are called the **cation** and **anion**, respectively, as shown in Figure 1.8. As a result of the Coulombic force, the two ions pull each other until the attractive force is just balanced by the repulsive force between the closed electron shells. Initially, energy is needed to remove the electron from the Na atom; this is the **energy of ionization**. However, this is more than compensated for by the energy of Coulombic attraction between the two resulting oppositely charged ions, and the net effect is a lowering of the potential energy of the Na^+ and Cl^- ion pair.

When many Na and Cl atoms are ionized and brought together, the resulting collection of ions is held together by the Coulombic attraction between the Na^+ and Cl^- ions. The solid thus consists of Na^+ cations and Cl^- anions holding each other through the Coulombic force, as depicted in Figure 1.9. The Coulombic force around a charge is nondirectional; also, it can be attractive or repulsive, depending on the polarity of the interacting ions. There are also repulsive Coulombic forces between the Na^+ ions themselves and between the Cl^- ions themselves. For the solid to be stable, each Na^+ ion must therefore have Cl^- ions as nearest neighbors and vice versa so that like-ions are not close to each other.

The ions are in equilibrium and the solid is stable when the net potential energy is minimum, or $dE/dr = 0$. Figure 1.10 illustrates the variation of the net potential

**Figure 1.9**

(a) A schematic illustration of a cross section from solid NaCl. Solid NaCl is made of Cl^- and Na^+ ions arranged alternately, so the oppositely charged ions are closest to each other and attract each other. There are also repulsive forces between the like-ions. In equilibrium, the net force acting on any ion is zero.

(b) Solid NaCl.

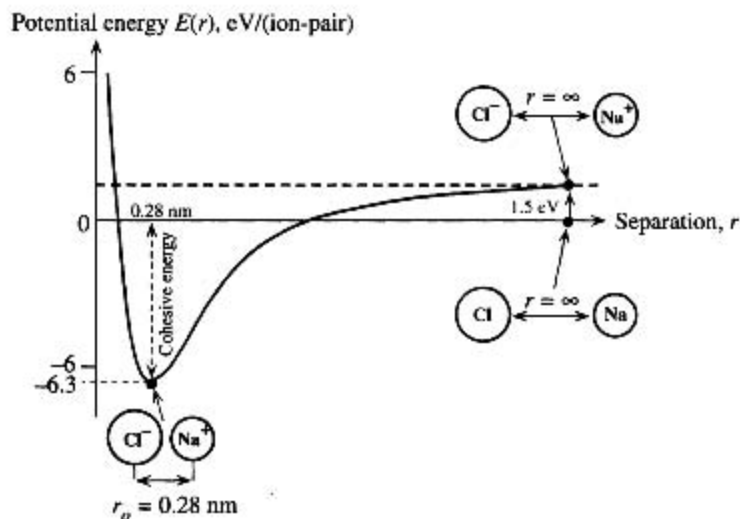


Figure 1.10 Sketch of the potential energy per ion pair in solid NaCl. Zero energy corresponds to neutral Na and Cl atoms infinitely separated.

energy for a pair of ions as the interatomic distance r is reduced from infinity to less than the equilibrium separation, that is, as the ions are brought together from infinity. Zero energy corresponds to separated Na and Cl atoms. Initially, about 1.5 eV is required to transfer the electron from the Na to Cl atom and thereby form Na^+ and Cl^- ions. Then, as the ions come together, the energy is lowered, until it reaches a

minimum at about 6.3 eV below the energy of the separated Na and Cl atoms. When $r = 0.28$ nm, the energy is minimum and the ions are in equilibrium. The bonding energy per ion in solid NaCl is thus 6.3/2 or 3.15 eV, as is apparent in Figure 1.10. The energy required to take solid NaCl apart into individual Na and Cl atoms is the **atomic cohesive energy** of the solid, which is 3.15 eV per atom.

In solid NaCl, the Na^+ and Cl^- ions are thus arranged with each one having oppositely charged ions as its neighbors, to attain a minimum of potential energy. Since there is a size difference between the ions and since we must avoid like-ions getting close to each other, if we want to achieve a stable structure, each ion can have only six oppositely charged ions as nearest neighbors. Figure 1.9b shows the packing of Na^+ and Cl^- ions in the solid. The number of nearest neighbors, that is, the **coordination number**, for both cations and anions in the NaCl crystal is 6.

A number of solids consisting of metal–nonmetal elements follow the NaCl example and have ionic bonding. They are called **ionic crystals** and, by virtue of their ionic bonding characteristics, share many physical properties. For example, LiF, MgO (magnesia), CsCl, and ZnS are all ionic crystals. They are strong, brittle materials with high melting temperatures compared to metals. Most become soluble in polar liquids such as water. Since all the electrons are within the rigidly positioned ions, there are no free or loose electrons to wander around in the crystal as in metals. Therefore, ionic solids are typically electrical insulators. Compared to metals and covalently bonded solids, ionically bonded solids have lower thermal conductivity since ions cannot readily pass vibrational kinetic energy to their neighbors.

IONIC BONDING AND LATTICE ENERGY The potential energy E per $\text{Na}^+ - \text{Cl}^-$ pair within the NaCl crystal depends on the interionic separation r as

$$E(r) = -\frac{e^2 M}{4\pi\epsilon_0 r} + \frac{B}{r^m} \quad [1.4]$$

where the first term is the *attractive* and the second term is the *repulsive* potential energy, and M , B , and m are constants explained in the following. If we were to consider the potential energy PE of one ion pair in isolation from all others, the first term would be a simple Coulombic interaction energy for the $\text{Na}^+ - \text{Cl}^-$ pair, and M would be 1. Within the NaCl crystal, however, a given ion, such as Na^+ , interacts not only with its nearest six Cl^- neighbors (Figure 1.9b), but also with its twelve second neighbors (Na^+), eight third neighbors (Cl^-), and so on, so the total or effective PE has a factor M , called the *Madelung constant*, that takes into account all these different Coulombic interactions. M depends only on the geometrical arrangement of ions in the crystal, and hence on the particular crystal structure; for the FCC crystal structure, $M = 1.748$. The $\text{Na}^+ - \text{Cl}^-$ ion pair also have a repulsive PE that is due to the repulsion between the electrons in filled electronic subshells of the ions. If the ions are pushed toward each other, the filled subshells begin to overlap, which results in a strong repulsion. The repulsive PE decays rapidly with distance and can be modeled by a short-range PE of the form B/r^m as in the second term in Equation 1.4 where for $\text{Na}^+ - \text{Cl}^-$, $m = 8$ and $B = 6.972 \times 10^{-96} \text{ J m}^8$. Find the equilibrium separation (r_0) of the ions in the crystal and the ionic bonding energy, defined as $-E(r_0)$. Given the *ionization energy* of Na (the energy to remove an electron) is 5.14 eV and the *electron affinity* of Cl (energy released when an electron is added) is 3.61 eV, calculate the *atomic cohesive energy* of the NaCl crystal as joules per mole.

EXAMPLE 1.3

Energy per ion pair in an ionic crystal

SOLUTION

Bonding occurs when the potential energy $E(r)$ is a minimum at $r = r_o$, corresponding to the equilibrium separation between the Na^+ and Cl^- ions. We differentiate $E(r)$ and set it to zero at $r = r_o$,

$$\frac{dE(r)}{dr} = \frac{e^2 M}{4\pi \epsilon_o r^2} - \frac{mB}{r^{m+1}} = 0 \quad \text{at } r = r_o$$

Solving for r_o ,

Equilibrium
ionic
separation

$$r_o = \left[\frac{4\pi \epsilon_o B m}{e^2 M} \right]^{1/(m-1)} \quad [1.5]$$

Thus,

$$\begin{aligned} r_o &= \left[\frac{4\pi (8.85 \times 10^{-12} \text{ F m}^{-1})(6.972 \times 10^{-96} \text{ J m}^8)(8)}{(1.6 \times 10^{-19} \text{ C})^2 (1.748)} \right]^{1/(8-1)} \\ &= 0.281 \times 10^{-9} \text{ m} \quad \text{or} \quad 0.28 \text{ nm} \end{aligned}$$

The minimum energy E_{\min} per ion pair is $E(r_o)$ and can be simplified further by substituting for B in terms of r_o :

Minimum PE
at bonding

$$E_{\min} = -\frac{e^2 M}{4\pi \epsilon_o r_o} + \frac{B}{r_o^m} = -\frac{e^2 M}{4\pi \epsilon_o r_o} \left(1 - \frac{1}{m} \right) \quad [1.6]$$

Thus,

$$\begin{aligned} E_{\min} &= -\frac{(1.6 \times 10^{-19} \text{ C})^2 (1.748)}{4\pi (8.85 \times 10^{-12} \text{ F m}^{-1})(2.81 \times 10^{-10} \text{ m})} \left(1 - \frac{1}{8} \right) \\ &= -1.256 \times 10^{-18} \text{ J} \quad \text{or} \quad -7.84 \text{ eV} \end{aligned}$$

This is the energy with respect to two isolated Na^+ and Cl^- ions. We need 7.84 eV to break up a $\text{Na}^+ - \text{Cl}^-$ pair into isolated Na^+ and Cl^- ions, which represents the *ionic cohesive energy*. Some authors call this ionic cohesive energy simply the **lattice energy**. To take the crystal apart into its neutral atoms, we have to transfer the electron from the Cl^- ion to the Na^+ ion to obtain neutral Na and Cl atoms. It takes 3.61 eV to remove the electron from the Cl^- ion, but 5.14 eV is released when it is put into the Na^+ ion. Thus, we need 7.84 eV + 3.61 eV but get back 5.14 eV.

$$\text{Bond energy per Na-Cl pair} = 7.84 \text{ eV} + 3.61 \text{ eV} - 5.14 \text{ eV} = 6.31 \text{ eV}$$

The *atomic cohesive energy* in terms of joules per mole is

$$E_{\text{cohesive}} = (6.31 \text{ eV})(1.6022 \times 10^{-19} \text{ J/eV})(6.022 \times 10^{23} \text{ mol}^{-1}) = 608 \text{ kJ mol}^{-1}$$

1.3.5 SECONDARY BONDING

Covalent, ionic, and metallic bonds between atoms are known as **primary bonds**. It may be thought that there should be no such bonding between the atoms of the inert elements as they have full shells and therefore cannot accept or lose any electrons, nor share any electrons. However, the fact that a solid phase of argon exists at low temperatures, below -189°C , means that there must be some bonding mechanism between the Ar atoms. The magnitude of this bond cannot be strong because above -189°C solid argon melts. Although each water molecule H_2O is neutral overall, these molecules nonetheless attract each other to form the liquid state below 100°C and the solid state below 0°C . Between all atoms and molecules, there exists a weak type of attraction, the

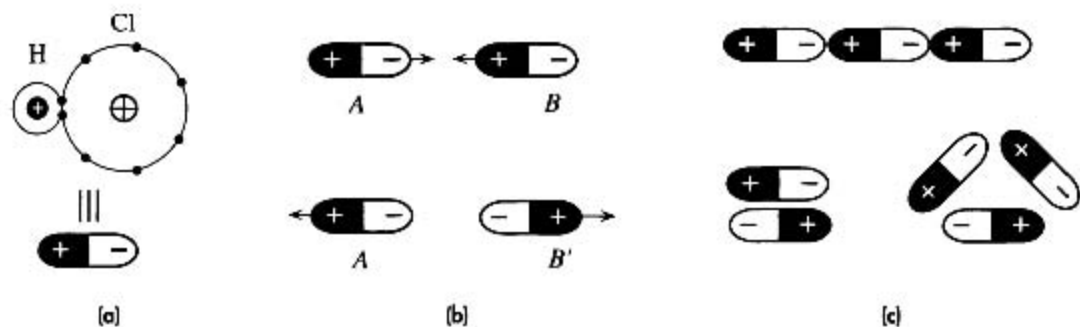


Figure 1.11

- (a) A permanently polarized molecule is called an electric dipole moment.
 (b) Dipoles can attract or repel each other depending on their relative orientations.
 (c) Suitably oriented dipoles attract each other to form van der Waals bonds.

so-called van der Waals–London force, which is due to a net electrostatic attraction between the electron distribution of one atom and the positive nucleus of the other.

In many molecules the concentrations of negative and positive charges do not coincide. As apparent in the HCl molecule in Figure 1.11a, the electrons spend most of their time around the Cl nucleus, so the positive nucleus of the H atom is exposed (H has effectively donated its electron to the Cl atom) and the Cl-region acquires more negative charge than the H-region. An **electric dipole moment** occurs whenever a negative and a positive charge of equal magnitude are separated by a distance as in the H^+-Cl^- molecule in Figure 1.11a. Such molecules are **polar**, and depending on their relative orientations, they can attract or repel each other as depicted in Figure 1.11b. Two dipoles arranged head to tail attract each other because the closest separation between charges on A and B is between the negative charge on A and the positive charge on B, and the *net* result is an electrostatic attraction. The magnitude of the *net force* between two dipoles A and B, however, does not depend on their separation r as $1/r^2$ because there are both attractions and repulsions between the charges on A and charges on B and the net force is only *weakly* attractive. (In fact, the net force depends on $1/r^4$.) If the dipoles are arranged head to head or tail to tail, then, by similar arguments, the two dipoles repel each other. Suitably arranged dipoles can attract each other and form **van der Waals bonds** as illustrated in Figure 1.11c. The energies of such dipole arrangements as in Figure 1.11c are less than that of totally isolated dipoles and therefore encourage “bonding.” Such bonds are weaker than primary bonds and are called **secondary bonds**.

The water molecule H_2O is also polar and has a net dipole moment as shown in Figure 1.12a. The attractions between the positive charges on one molecule and the negative charges on a neighboring molecule lead to van der Waals bonding between the H_2O molecules in water as illustrated in Figure 1.12b. When the positive charge of a dipole as in H_2O arises from an exposed H nucleus, van der Waals bonding is referred to as **hydrogen bonding**. In ice, the H_2O molecules, again attracted by van der Waals forces, bond to form a regular pattern and hence a crystal structure.

Van der Waals attraction also occurs between neutral atoms and nonpolar molecules. Consider the bonding between Ne atoms at low temperatures. Each has closed (or full) electron shells. The center of mass of the electrons in the closed shells, when

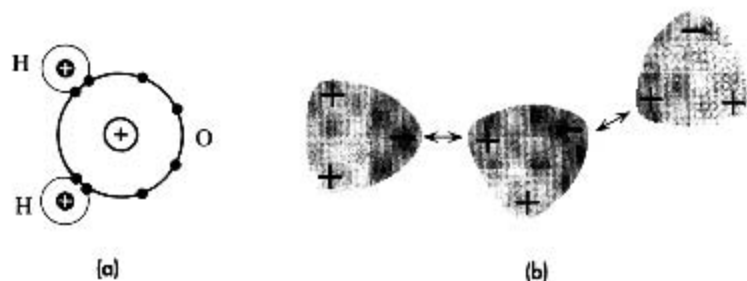


Figure 1.12 The origin of van der Waals bonding between water molecules. (a) The H_2O molecule is polar and has a net permanent dipole moment. (b) Attractions between the various dipole moments in water give rise to van der Waals bonding.

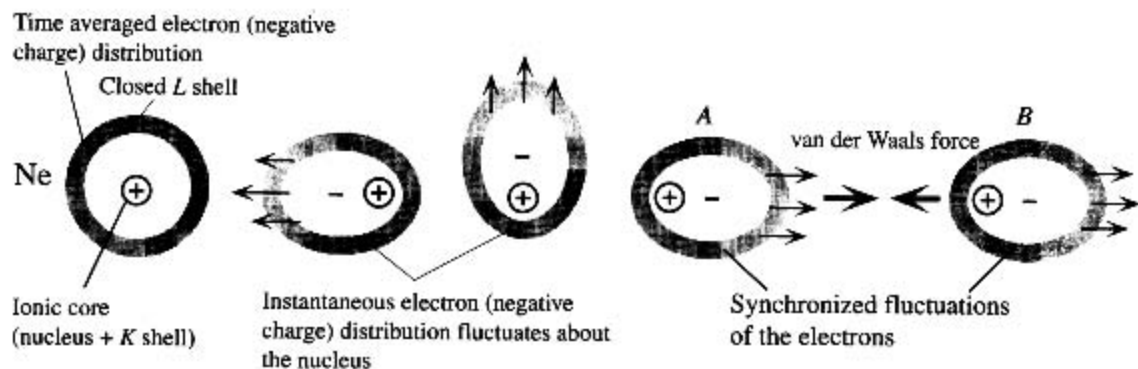


Figure 1.13 Induced-dipole-induced-dipole interaction and the resulting van der Waals force.

averaged over time, coincides with the location of the positive nucleus. At any one instant, however, the center of mass is displaced from the nucleus due to various motions of the individual electrons around the nucleus as depicted in Figure 1.13. In fact, the center of mass of all the electrons fluctuates with time about the nucleus. Consequently, the electron charge distribution is not static around the nucleus but fluctuates asymmetrically, giving rise to an instantaneous dipole moment.

When two Ne atoms, *A* and *B*, approach each other, the rapidly fluctuating negative charge distribution on one affects the motion of the negative charge distribution on the other. A lower energy configuration (*i.e.*, attraction) is produced when the fluctuations are synchronized so that the negative charge distribution on *A* gets closer to the nucleus of the other, *B*, while the negative distribution on *B* at that instant stays away from that on *A* as shown in Figure 1.13. The strongest electrostatic interaction arises from the closest charges which are the displaced electrons in *A* and the nucleus in *B*. This means that there will be a *net* attraction between the two atoms and hence a lowering of the net energy which in turn leads to bonding.

This type of attraction between two atoms is due to induced synchronization of the electronic motions around the nuclei, and we refer to this as *induced-dipole-induced-*

Table 1.2 Comparison of bond types and typical properties [general trends]

Bond Type	Typical Solids	Bond Energy (eV/atom)	Melt. Temp. (°C)	Elastic Modulus (GPa)	Density (g cm ⁻³)	Typical Properties
Ionic	NaCl (rock salt)	3.2	801	40	2.17	Generally electrical insulators. May become conductive at high temperatures.
	MgO (magnesia)	10	2852	250	3.58	High elastic modulus. Hard and brittle but cleavable. Thermal conductivity less than metals.
Metallic	Cu	3.1	1083	120	8.96	Electrical conductor.
	Mg	1.1	650	44	1.74	Good thermal conduction. High elastic modulus. Generally ductile. Can be shaped.
Covalent	Si	4	1410	190	2.33	Large elastic modulus. Hard and brittle.
	C (diamond)	7.4	3550	827	3.52	Diamond is the hardest material. Good electrical insulator. Moderate thermal conduction, though diamond has exceptionally high thermal conductivity.
van der Waals: hydrogen bonding	PVC (polymer)		212	4	1.3	Low elastic modulus. Some ductility.
	H ₂ O (ice)	0.52	0	9.1	0.917	Electrical insulator. Poor thermal conductivity. Large thermal expansion coefficient.
van der Waals: induced dipole	Crystalline argon	0.09	-189	8	1.8	Low elastic modulus. Electrical insulator. Poor thermal conductivity. Large thermal expansion coefficient.

dipole. It is weaker than permanent dipole interactions and at least an order of magnitude less than primary bonding. This is the reason why the inert elements Ne and Ar solidify at temperatures below 25 K (-248 °C) and 84 K (-189 °C). Induced dipole-induced dipole interactions also occur between nonpolar molecules such as H₂, I₂, CH₄, etc. Methane gas (CH₄) can be solidified at very low temperatures. Solids in which constituent molecules (or atoms) have been bonded by van der Waals forces are known as **molecular solids**; ice, solidified CO₂ (dry ice), O₂, H₂, CH₄, and solid inert gases, are typical examples.

Van der Waals bonding is responsible for holding the carbon chains together in polymers. Although the C-to-C bond in a C-chain is due to covalent bonding, the interaction between the C-chains arises from van der Waals forces and the interchain bonding is therefore of secondary nature. These bonds are weak and can be easily stretched or broken. Polymers therefore have substantially lower elastic moduli and melting temperatures than metals and ceramics.

Table 1.2 compares the energies involved in the five types of bonding found in materials. It also lists some important properties of these materials to show the correlation

with the bond type and its energy. The greater is the bond energy, for example, the higher is the melting temperature. Similarly, strong bond energies lead to greater elastic moduli and smaller thermal expansion coefficients. Metals generally have the greatest electrical conductivity since only this type of bonding allows a very large number of free charges (conduction electrons) to wander in the solid and thereby contribute to electrical conduction. Electrical conduction in other types of solid may involve the motion of ions or charged defects from one fixed location to another.

1.3.6 MIXED BONDING

In many solids, the bonding between atoms is generally not just of one type; rather, it is a mixture of bond types. We know that bonding in the silicon crystal is totally covalent, because the shared electrons in the bonds are equally attracted by the neighboring positive ion cores and are therefore equally shared. When there is a covalent-type bond between two different atoms, the electrons become unequally shared, because the two neighboring ion cores are different and hence have different electron-attracting abilities. The bond is no longer purely covalent; it has some ionic character, because the shared electrons spend more time close to one of the ion cores. Covalent bonds that have an ionic character, due to an unequal sharing of electrons, are generally called **polar bonds**. Many technologically important semiconductor materials, such as III-V compounds (e.g., GaAs), have polar covalent bonds. In GaAs, for example, the electrons in a covalent bond spend slightly more time around the As^{5+} ion core than the Ga^{+3} ion core.

Electronegativity is a relative measure of the ability of an atom to attract the electrons in a bond it forms with another atom. The *Pauling scale of electronegativity* assigns an electronegativity value X , a pure number, to various elements, the highest being 4 for F, and the lowest values being for the alkali metal atoms, for which X are less than 1. In this scheme, the difference $X_A - X_B$ in the electronegativities of two atoms A and B is a measure of the polar or ionic character of the bond $A-B$ between A and B . There is obviously no electronegativity difference for a covalent bond. While it is possible to calculate the fractional ionicity of a single bond between two different atoms using $X_A - X_B$, inside the crystal the overall ionic character can be substantially higher because ions can interact with distant ions further away than just the nearest neighbors, as we have found out in NaCl. Many technologically important semiconductor materials, such as III-V compounds (e.g., GaAs) have polar covalent bonds. In GaAs, for example, the bond in the crystal is about 30 percent ionic in character ($X_{\text{As}} - X_{\text{Ga}} = 2.18 - 1.81 = 0.37$). In the ZnSe crystal, an important II-VI semiconductor, the bond is 63 percent ionic ($X_{\text{Se}} - X_{\text{Zn}} = 2.55 - 1.65 = 0.85$).⁶

Ceramic materials are compounds that generally contain metallic and nonmetallic elements. They are well known for their brittle mechanical properties, hardness, high

⁶ Chemists use "ionicity = $1 - \exp[0.24(X_A - X_B)]$ " to calculate the ionicity of the bond between A and B . While this is undoubtedly useful in identifying the trend, it substantially underestimates the actual ionicity of bonding within the crystal itself. (It is left as an exercise to show this fact from the above X_A and X_B values.) The quoted ionicity percentages are from J. C. Phillips' book *Bonds and Bands in Semiconductors*, New York: Academic Press, 1973. By the way, the units of X are sometimes quoted as Pauling units, after its originator Linus Pauling.

melting temperatures, and electrical insulating properties. The type of bonding in a ceramic material may be covalent, ionic, or a mixture of the two, in which the bond between the atoms involves some electron sharing and, to some extent, the partial formation of cations and anions; the shared electrons spend more time with one type of atom, which then becomes a partial anion while the other becomes a partial cation. Silicon nitride (Si_3N_4), magnesia (MgO), and alumina (Al_2O_3) are all ceramics, but they have different types of bonding: Si_3N_4 has covalent, MgO has ionic, and Al_2O_3 has a mixture of ionic and covalent bonding. All three are brittle, have high melting temperatures, and are electrical insulators.

ENERGY OF SECONDARY BONDING Consider the van der Waals bonding in solid argon. The potential energy as a function of interatomic separation can generally be modeled by the Lennard–Jones 6–12 potential energy curve, that is,

EXAMPLE 1.4

$$E(r) = -Ar^{-6} + Br^{-12}$$

where A and B are constants. Given that $A = 8.0 \times 10^{-77} \text{ J m}^6$ and $B = 1.12 \times 10^{-133} \text{ J m}^{12}$, calculate the bond length and bond energy (in eV) for solid argon.

SOLUTION

Bonding occurs when the potential energy is at a minimum. We therefore differentiate the Lennard–Jones potential $E(r)$ and set it to zero at $r = r_o$, the interatomic equilibrium separation or

$$\frac{dE}{dr} = 6Ar^{-7} - 12Br^{-13} = 0 \quad \text{at } r = r_o$$

that is,

$$r_o^6 = \frac{2B}{A}$$

or

$$r_o = \left[\frac{2B}{A} \right]^{1/6}$$

Substituting $A = 8.0 \times 10^{-77}$ and $B = 1.12 \times 10^{-133}$ and solving for r_o , we find

$$r_o = 3.75 \times 10^{-10} \text{ m} \quad \text{or} \quad 0.375 \text{ nm}$$

When $r = r_o = 3.75 \times 10^{-10} \text{ m}$, the potential energy is at a minimum and corresponds to $-E_{\text{bond}}$, so

$$E_{\text{bond}} = \left| -Ar_o^{-6} + Br_o^{-12} \right| = \left| -\frac{8.0 \times 10^{-77}}{(3.75 \times 10^{-10})^6} + \frac{1.12 \times 10^{-133}}{(3.75 \times 10^{-10})^{12}} \right|$$

that is,

$$E_{\text{bond}} = 1.43 \times 10^{-20} \text{ J} \quad \text{or} \quad 0.089 \text{ eV}$$

Notice how small this energy is compared to primary bonding.

EXAMPLE 1.5

ELASTIC MODULUS The elastic modulus, or Young's modulus Y , of a solid indicates its ability to deform elastically. The greater is the elastic modulus, the more effort is required for the same amount of elastic deformation given a constant sample geometry. When a solid is subjected to tensile forces F acting on two opposite faces, as in Figure 1.14a, it experiences a stress σ defined as the force per unit area F/A , where A is the area on which F acts. If the original length of the specimen is L_o , then the applied stress σ stretches the solid by an amount δL . The strain ϵ is the fractional increase in the length of the solid $\delta L/L_o$. As long as the applied force displaces the atoms in the solid by a small amount from their equilibrium positions, the deformation is elastic and recoverable when the forces are removed. The applied stress σ and the resulting elastic strain ϵ are related by the elastic modulus Y by

$$\sigma = Y\epsilon \quad [1.7]$$

Definition of
elastic
modulus

The applied stress causes two neighboring atoms along the direction of force to be further separated. Their displacement $\delta r (= r - r_o)$ results in a net attractive force δF_N between two neighboring atoms as indicated in Figure 1.14b (which is the same as Figure 1.3a) where F_N is the net interatomic force. δF_N attempts to restore the separation to equilibrium. This force δF_N , however, is balanced by a portion of the applied force acting on these atoms as in Figure 1.14a. If we were to proportion the area A in Figure 1.14a among all the atoms on this area, each atom would have an area roughly r_o^2 . (If there are N atoms on A , $Nr_o^2 = A$.) The force δF_N is therefore σr_o^2 . The strain ϵ is $\delta r/r_o$. Thus, Equation 1.7 gives

$$\frac{\delta F_N}{r_o^2} = \sigma = Y \frac{\delta r}{r_o}$$

Clearly, Y depends on the gradient of the F_N versus r curve at r_o , or the curvature of the minimum of E versus r at r_o .

Elastic
modulus and
bonding

$$Y = \frac{1}{r_o} \left[\frac{dF_N}{dr} \right]_{r=r_o} = \frac{1}{r_o} \left[\frac{d^2E}{dr^2} \right]_{r=r_o} \quad [1.8]$$

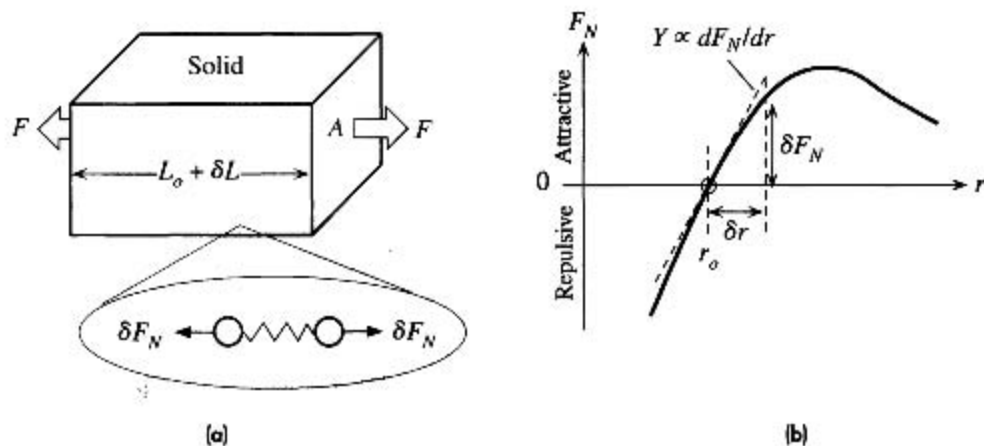


Figure 1.14

(a) Applied forces F stretch the solid elastically from L_o to $L_o + \delta L$. The force is divided among chains of atoms that make the solid. Each chain carries a force δF_N .

(b) In equilibrium, the applied force is balanced by the net force δF_N between the atoms as a result of their increased separation.

The bonding energy E_{bond} is the minimum of E versus r at r_o (Figure 1.3b) and can be related to the curvature of E versus r which leads to⁷

$$Y \approx f \frac{E_{\text{bond}}}{r_o^3} \quad [1.9]$$

*Elastic
modulus and
bond energy*

where f is a numerical factor (constant) that depends on the crystal structure and the type of bond (of the order of unity). The well-known Hooke's law for a spring expresses the magnitude of the net force δF_N in terms of the displacement δr by $\delta F_N = \beta|\delta r|$ where β is the spring constant. Thus $Y = \beta/r_o$.

Solids with higher bond energies therefore tend to have higher elastic moduli as apparent in Table 1.2. Secondary bonding has both a smaller E_{bond} and a larger r_o than primary bonding and Y is much smaller. For NaCl, from Figure 1.10, $E_{\text{bond}} = 6.3$ eV, $r_o = 0.28$ nm, and Y is of the order of ~ 50 GPa using Equation 1.9 and $f \approx 1$; and not far out from the value in Table 1.2.

1.4 KINETIC MOLECULAR THEORY

1.4.1 MEAN KINETIC ENERGY AND TEMPERATURE

The kinetic molecular theory of matter is a classical theory that can explain such seemingly diverse topics as the pressure of a gas, the heat capacity of metals, the average speed of electrons in a semiconductor, and electrical noise in resistors, among many interesting phenomena. We start with the kinetic molecular theory of gases, which considers a collection of gas molecules in a container and applies the classical equations of motion from elementary mechanics to these molecules. We assume that the collisions between the gas molecules and the walls of the container result in the gas pressure P . Newton's second law, $dp/dt = \text{force}$, where $p = mv$ is the momentum, is used to relate the pressure P (force per unit area) to the mean square velocity $\overline{v^2}$, and the number of molecules per unit volume N/V . The result can be stated simply as

$$PV = \frac{1}{3}Nm\overline{v^2} \quad [1.10]$$

*Kinetic
molecular
theory for
gases*

where m is the mass of the gas molecule. Comparing this theoretical derivation with the experimental observation that

$$PV = \left(\frac{N}{N_A}\right)RT$$

where N_A is **Avogadro's number** and R is the gas constant, we can relate the mean kinetic energy of the molecules to the temperature. Our objective is to derive Equation 1.10; to do so, we make the following assumptions:

1. The molecules are in constant random motion. Since we are considering a large number of molecules, perhaps 10^{20} m^{-3} , there are as many molecules traveling in one direction as in any other direction, so the center of mass of the gas is at rest.

⁷ The mathematics and a more rigorous description may be found in the textbook's CD.

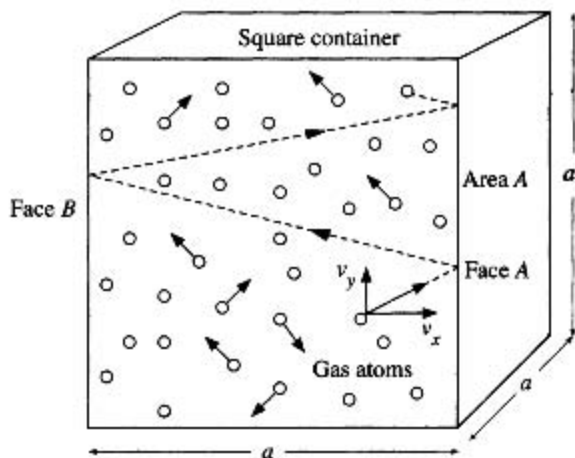
2. The range of intermolecular forces is short compared to the average separation of the gas molecules. Consequently,
 - a. Intermolecular forces are negligible, except during a collision.
 - b. The volume of the gas molecules (all together) is negligible compared to the volume occupied by the gas (that is, the container).
3. The duration of a collision is negligible compared to the time spent in free motion between collisions.
4. Each molecule moves with uniform velocity between collisions, and the acceleration due to the gravitational force or other external forces is neglected.
5. On average, the collisions of the molecules with one another and with the walls of the container are perfectly elastic. Collisions between molecules result in exchanges of kinetic energy.
6. Newtonian mechanics can be applied to describe the motion of the molecules.

We consider a collection of N gas molecules within a cubic container of side a . We focus our attention on one of the molecules moving toward one of the walls. The velocity can be decomposed into two components, one directly toward the wall v_x , and the other parallel to the wall v_y , as shown in Figure 1.15. Clearly, the collision of the molecule, which is perfectly elastic, does not change the component v_y along the wall, but reverses the perpendicular component v_x . The change in the momentum of the molecule following its collision with the wall is

$$\Delta p = 2mv_x$$

where m is the mass of the molecule. Following its collision, the molecule travels back across the box, collides with the opposite face B , and returns to hit face A again. The time interval Δt is the time to traverse twice the length of the box, or $\Delta t = 2a/v_x$. Thus, every Δt seconds, the molecule collides with face A and changes its momentum by $2mv_x$. To find the force F exerted by this molecule on face A , we need the rate of

Figure 1.15 The gas molecules in the container are in random motion.



change of momentum, or

$$F = \frac{\Delta p}{\Delta t} = \frac{2mv_x}{(2a/v_x)} = \frac{mv_x^2}{a}$$

The total pressure P exerted by N molecules on face A , of area a^2 , is due to the sum of all individual forces F , or

$$\begin{aligned} P &= \frac{\text{Total force}}{a^2} = \frac{mv_{x1}^2 + mv_{x2}^2 + \cdots + mv_{xN}^2}{a^3} \\ &= \frac{m}{a^3} (v_{x1}^2 + v_{x2}^2 + \cdots + v_{xN}^2) \end{aligned}$$

that is,

$$P = \frac{mN\overline{v_x^2}}{V}$$

where $\overline{v_x^2}$ is the average of v_x^2 for all the molecules and is called the *mean square velocity*, and V is the volume a^3 .

Since the molecules are in random motion and collide randomly with each other, thereby exchanging kinetic energy, the mean square velocity in the x direction is the same as those in the y and z directions, or

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2}$$

For any molecule, the velocity v is given by

$$\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2} = 3\overline{v_x^2}$$

The relationship between the pressure P and the mean square velocity of the molecules is therefore

$$P = \frac{Nm\overline{v^2}}{3V} = \frac{1}{3}\rho\overline{v^2} \quad [1.11]$$

*Gas pressure
in the kinetic
theory*

where ρ is the density of the gas, or Nm/V . By using elementary mechanical concepts, we have now related the pressure exerted by the gas to the number of molecules per unit volume and to the mean square of the molecular velocity.

Equation 1.11 can be written explicitly to show the dependence of PV on the mean kinetic energy of the molecules. Rearranging Equation 1.11, we obtain

$$PV = \frac{2}{3}N\left(\frac{1}{2}m\overline{v^2}\right)$$

where $\frac{1}{2}m\overline{v^2}$ is the average kinetic energy \overline{KE} per molecule. If we consider one mole of gas, then N is simply N_A , Avogadro's number.

Experiments on gases lead to the empirical gas equation

$$PV = \left(\frac{N}{N_A}\right)RT$$

where R is the universal gas constant. Comparing this equation with the kinetic theory equation shows that the average kinetic energy per molecule must be proportional to

the temperature.

Mean kinetic energy per atom

$$\overline{KE} = \frac{1}{2} m \overline{v^2} = \frac{3}{2} kT \quad (1.12)$$

where $k = R/N_A$ is called the **Boltzmann constant**. Thus, the mean square velocity is proportional to the absolute temperature. This is a major conclusion from the kinetic theory, and we will use it frequently.

When heat is added to a gas, its internal energy and, by virtue of Equation 1.12, its temperature both increase. The rise in the internal energy per unit temperature is called the **heat capacity**. If we consider 1 mole of gas, then the heat capacity is called the **molar heat capacity** C_m . The total internal energy U of 1 mole of monatomic gas (i.e., a gas with only one atom in each molecule) is

$$U = N_A \left(\frac{1}{2} m \overline{v^2} \right) = \frac{3}{2} N_A k T$$

so, from the definition of C_m , at constant volume, we have

$$C_m = \frac{dU}{dT} = \frac{3}{2} N_A k = \frac{3}{2} R \quad (1.13)$$

Molar heat capacity at constant volume

Thus, the heat capacity per mole of a monatomic gas at constant volume is simply $\frac{3}{2}R$. By comparison, we will see later that the heat capacity of metals is twice this amount. The reason for considering constant volume is that the heat added to the system then increases the internal energy without doing mechanical work by expanding the volume.

There is a useful theorem called **Maxwell's principle of equipartition of energy**, which assigns an average of $\frac{1}{2}kT$ to each independent energy term in the expression for the total energy of a system. A monatomic molecule can only have translational kinetic energy, which is the sum of kinetic energies in the x , y , and z directions. The total energy is therefore

$$E = \frac{1}{2} m v_x^2 + \frac{1}{2} m v_y^2 + \frac{1}{2} m v_z^2$$

Each of these terms represents an independent way in which the molecule can be made to absorb energy. Each method by which a system can absorb energy is called a **degree of freedom**. A monatomic molecule has only three degrees of freedom. According to Maxwell's principle, for a collection of molecules in thermal equilibrium, each degree of freedom has an average energy of $\frac{1}{2}kT$, so the average kinetic energy of the monatomic molecule is $3(\frac{1}{2}kT)$.

A rigid diatomic molecule (such as an O_2 molecule) can acquire energy as translational motion and rotational motion, as depicted in Figure 1.16. Assuming the moment of inertia I_x about the molecular axis (along x) is negligible, the energy of the molecule is

$$E = \frac{1}{2} m v_x^2 + \frac{1}{2} m v_y^2 + \frac{1}{2} m v_z^2 + \frac{1}{2} I_y \omega_y^2 + \frac{1}{2} I_z \omega_z^2$$

where I_y and I_z are moments of inertia about the y and z axes and ω_y and ω_z are angular velocities about the y and z axes (Figure 1.16).

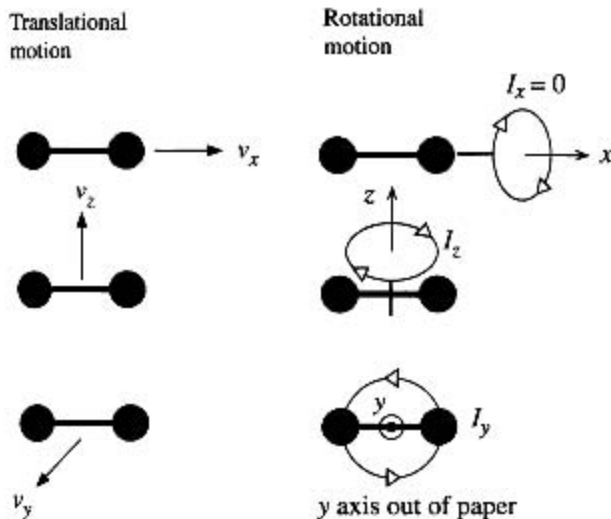


Figure 1.16 Possible translational and rotational motions of a diatomic molecule. Vibrational motions are neglected.

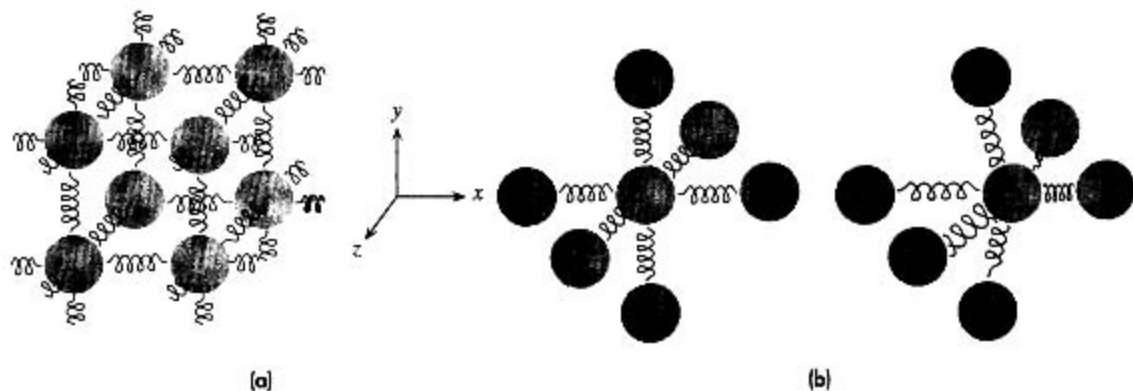
This molecule has five degrees of freedom and hence an average energy of $5(\frac{1}{2}kT)$. Its molar heat capacity is therefore $\frac{5}{2}R$.

The atoms in the molecule will also vibrate by stretching or bending the bond, which behaves like a "spring." At room temperature, the addition of heat only results in the translational and rotational motions becoming more energetic (excited), whereas the molecular vibrations remain the same and therefore do not absorb energy. This occurs because the vibrational energy of the molecule can only change in finite steps; in other words, the vibrational energy is quantized. For many molecules, the energy required to excite a more energetic vibration is much more than the energy possessed by the majority of molecules. Therefore, energy exchanges via molecular collisions cannot readily excite more energetic vibrations; consequently, the contribution of molecular vibrations to the heat capacity is negligible.

In a solid, the atoms are bonded to each other and can only move by vibrating about their equilibrium positions. In the simplest view, a typical atom in a solid is joined to its neighbors by "springs" that represent the bonds, as depicted in Figure 1.17. If we consider a given atom, its potential energy as a function of displacement from the equilibrium position is such that if it is displaced slightly in any direction, it will experience a restoring force proportional to the displacement. Thus, this atom can acquire energy by vibrations in three directions. The energy associated with the x direction, for example, is the kinetic energy of vibration plus the potential energy of the "spring," or $\frac{1}{2}mv_x^2 + \frac{1}{2}K_x x^2$, where v_x is the velocity, x is the extension of the spring, and K_x is the spring constant, all along the x direction. Clearly, there are similar energy terms in the y and z directions, so there are six energy terms in the total energy equation:

$$E = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 + \frac{1}{2}K_x x^2 + \frac{1}{2}K_y y^2 + \frac{1}{2}K_z z^2$$

We know that for simple harmonic motion, the average KE is equal to the average PE . Since, by virtue of the equipartition of energy principle, each average KE term has

**Figure 1.17**

(a) The ball-and-spring model of solids, in which the springs represent the interatomic bonds. Each ball (atom) is linked to its neighbors by springs. Atomic vibrations in a solid involve three dimensions.

(b) An atom vibrating about its equilibrium position. The atom stretches and compresses its springs to its neighbors and has both kinetic and potential energy.

an energy of $\frac{1}{2}kT$, the average total energy per atom is $6(\frac{1}{2}kT)$. The internal energy U per mole is

$$U = N_A 6 \left(\frac{1}{2} kT \right) = 3RT$$

The molar heat capacity then becomes

$$C_m = \frac{dU}{dT} = 3R = 25 \text{ J K}^{-1} \text{ mol}^{-1}$$

*Dulong–Petit
rule*

This is the **Dulong–Petit rule**.

The kinetic molecular theory of matter is one of the successes of classical physics, with a beautiful simplicity in its equations and predictions. Its failures, however, are numerous. For example, the theory fails to predict that, at low temperatures, the heat capacity increases as T^3 and that the resistivity of a metal increases linearly with the absolute temperature. We will explain the origins of these phenomena in Chapter 4.

EXAMPLE 1.6

SPEED OF SOUND IN AIR Calculate the root mean square (rms) velocity of nitrogen molecules in atmospheric air at 27 °C. Also calculate the root mean square velocity in one direction ($v_{\text{rms},x}$). Compare the speed of propagation of sound waves in air, 350 m s^{-1} , with $v_{\text{rms},x}$ and explain the difference.

SOLUTION

From the kinetic theory

$$\frac{1}{2} m v_{\text{rms}}^2 = \frac{3}{2} kT$$

so that

$$v_{\text{rms}} = \sqrt{\frac{3kT}{m}}$$

where m is the mass of the nitrogen molecule N_2 . The atomic mass of nitrogen is $M_{\text{at}} = 14 \text{ g mol}^{-1}$, so that in kilograms

$$m = \frac{2M_{\text{at}}(10^{-3})}{N_A}$$

Thus

$$\begin{aligned} v_{\text{rms}} &= \left[\frac{3kN_A T}{2M_{\text{at}}(10^{-3})} \right]^{1/2} = \left[\frac{3RT}{2M_{\text{at}}(10^{-3})} \right]^{1/2} \\ &= \left[\frac{3(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(300 \text{ K})}{2(14 \times 10^{-3} \text{ kg mol}^{-1})} \right]^{1/2} = 517 \text{ m s}^{-1} \end{aligned}$$

Consider an rms velocity in one direction. Then

$$v_{\text{rms},x} = \sqrt{v_x^2} = \sqrt{\frac{1}{3}v^2} = \frac{1}{\sqrt{3}}v_{\text{rms}} = 298 \text{ m s}^{-1}$$

which is slightly less than the velocity of sound in air (350 m s^{-1}). The difference is due to the fact that the propagation of a sound wave involves rapid compressions and rarefactions of air, and the result is that the propagation is not isothermal. Note that accounting for oxygen in air lowers $v_{\text{rms},x}$. (Why?)

SPECIFIC HEAT CAPACITY Estimate the heat capacity of copper per unit gram, given that its atomic mass is 63.6.

EXAMPLE 1.7

SOLUTION

From the Dulong–Petit rule, $C_m = 3R$ for N_A atoms. But N_A atoms have a mass of M_{at} grams, so the heat capacity per gram, the specific heat capacity c_s , is

$$\begin{aligned} c_s &= \frac{3R}{M_{\text{at}}} = \frac{25 \text{ J mol}^{-1} \text{ K}^{-1}}{63.6 \text{ g mol}^{-1}} \\ &\approx 0.39 \text{ J g}^{-1} \text{ K}^{-1} \quad (\text{The experimental value is } 0.38 \text{ J g}^{-1} \text{ K}^{-1}.) \end{aligned}$$

1.4.2 THERMAL EXPANSION

Nearly all materials expand as the temperature increases. This phenomenon is due to the asymmetric nature of the interatomic forces and the increase in the amplitude of atomic vibrations with temperature as expected from the kinetic molecular theory.

The potential energy curve $U(r)$ for two atoms separated by a distance r is shown in Figure 1.18. In equilibrium the PE is a minimum at $U_{\text{min}} = -U_o$ and the bonding energy is simply U_o . The atoms are separated by the equilibrium separation r_o . However,

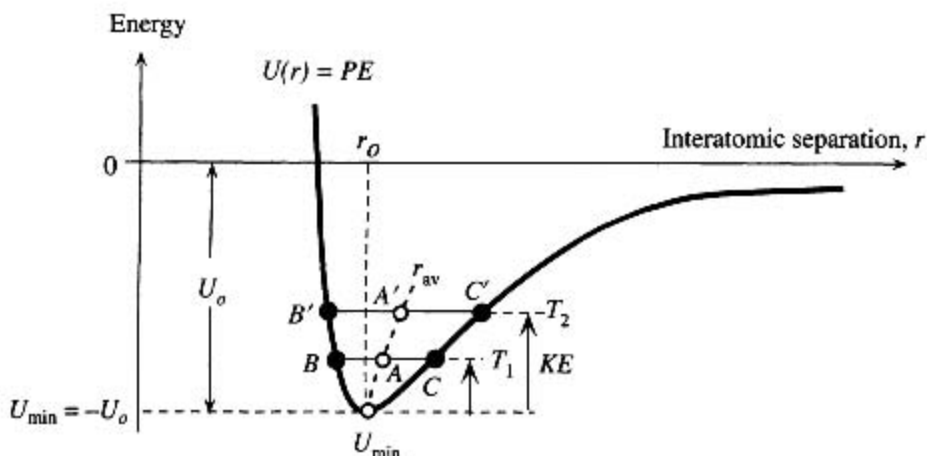


Figure 1.18 The potential energy PE curve has a minimum when the atoms in the solid attain the interatomic separation at $r = r_0$.

Because of thermal energy, the atoms will be vibrating and will have vibrational kinetic energy. At $T = T_1$, the atoms will be vibrating in such a way that the bond will be stretched and compressed by an amount corresponding to the KE of the atoms. A pair of atoms will be vibrating between B and C . Their average separation will be at A and greater than r_0 .

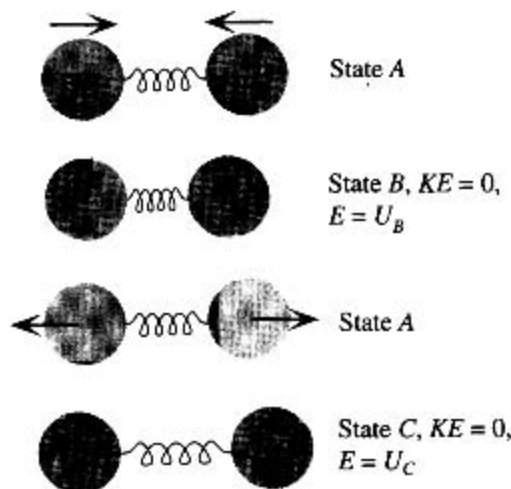


Figure 1.19 Vibrations of atoms in the solid. We consider for simplicity a pair of atoms. Total energy is $E = PE + KE$, and this is constant for a pair of vibrating atoms executing simple harmonic motion. At B and C , KE is zero (atoms are stationary and about to reverse direction of oscillation) and PE is maximum.

according to the kinetic molecular theory, atoms are vibrating about their equilibrium positions with a mean vibrational kinetic energy that increases with the temperature as $\frac{3}{2}kT$. At any instant the total energy E of the pair of atoms is $U + KE$, and this is constant inasmuch as no external forces are being applied. The atoms will be vibrating about their equilibrium positions, stretching and compressing the bond, as depicted in Figure 1.19. At positions B and C , U is maximum and the KE is zero; the atoms are stationary and about to reverse their direction of oscillation. Thus at B and C the total

energy $E = U_B = U_C$ and the PE has increased from its minimum value U_{\min} by an amount equal to KE . The line BC corresponds to the total energy E . The atoms are confined to vibrate between B and C , executing simple harmonic motion and hence maintaining $E = U + KE = \text{constant}$.

But the PE curve $U(r)$ is *asymmetric*. $U(r)$ is broader in the $r > r_o$ region. Thus, the atoms spend more time in the $r > r_o$ region, that is, more time stretching the bond than compressing the bond (with respect to the equilibrium length r_o). The average separation corresponds to point A ,

$$r_{av} = \frac{1}{2}(r_B + r_C)$$

which is clearly greater than r_o . As the temperature increases, KE increases, the total energy E increases, and the atoms vibrate between wider extremes of the $U(r)$ curve, between B' and C' . The new average separation at A' is now greater than that at A : $r_{A'} > r_A$. Thus as the temperature increases, the average separation between the atoms also increases, which leads to the phenomenon of **thermal expansion**. If the PE curve were symmetric, then there would be no thermal expansion as the atoms would spend equal times in the $r < r_o$ and $r > r_o$ regions.

When the temperature increases by a small amount δT , the energy per atom increases by $C_{\text{atom}} \delta T$ where C_{atom} is the heat capacity per atom (molar heat capacity divided by N_A). If $C_{\text{atom}} \delta T$ is large, then the line $B'C'$ in Figure 1.18 will be higher up on the energy curve and the average separation A' will therefore be larger. Thus, the increase δr_{av} in the average separation is proportional to δT . If the total length L_o is made up of N atoms, $L_o = N r_{av}$, then the change δL in L_o is proportional to $N \delta T$ or $L_o \delta T$. The proportionality constant is the **thermal coefficient of linear expansion**, or simply, **thermal expansion coefficient** λ , which is defined as the fractional change in length per unit temperature,

$$\lambda = \frac{1}{L_o} \cdot \frac{\delta L}{\delta T} \quad [1.14]$$

Definition of thermal expansion coefficient

If L_o is the original length at temperature T_o , then the length L at temperature T , from Equation 1.14, is

$$L = L_o[1 + \lambda(T - T_o)] \quad [1.15]$$

Thermal expansion

We note that λ is a material property that depends on the nature of the bond. The variation of r_{av} with T in Figure 1.18 depends on the shape of the PE curve $U(r)$. Typically, λ is larger for metallic bonding than for covalent bonding.

We can use a mathematical procedure (known as a Taylor expansion) to describe the $U(r)$ versus r curve in terms of its minimum value U_{\min} , plus correction terms that depend on the powers of the *displacement* ($r - r_o$) from r_o ,

$$U(r) = U_{\min} + a_2(r - r_o)^2 + a_3(r - r_o)^3 + \dots \quad [1.16]$$

Potential energy of an atom

where a_2 and a_3 are coefficients that are related to the second and third derivatives of U at r_o . The term $a_1(r - r_o)$ is missing because $dU/dr = 0$ at $r = r_o$ where $U = U_{\min}$. The U_{\min} and $a_2(r - r_o)^2$ terms in Equation 1.16 give a parabola about U_{\min} which is a symmetric curve around r_o and therefore does not lead to thermal expansion. The average

location at any energy on a symmetric curve at r_0 is always at r_0 . It is the a_3 term that gives the expansion because it leads to asymmetry. Thus, λ depends on the amount of asymmetry, that is, a_3/a_2 . The asymmetric PE curve in Figure 1.18 which has a finite cubic a_3 term as in Equation 1.16 does not lead to a perfect simple harmonic (sinusoidal) vibration about r_0 because the restoring force is not proportional to the displacement alone. Such oscillations are **unharmonic**, and the PE curve is said to possess an **unharmonicity** (terms such as a_3). Thermal expansion is an **unharmonic effect**.

The thermal expansion coefficient normally depends on the temperature, $\lambda = \lambda(T)$, and typically increases with increasing temperature, except at the lowest temperatures. We can always expand $\lambda(T)$ about some useful temperature such as T_0 to obtain a polynomial series in temperature terms up to the most significant term, usually the T^2 containing term. Thus, Equation 1.14 becomes

$$\frac{dL}{L_0 dT} = \lambda(T) = A + B(T - T_0) + C(T - T_0)^2 + \dots \quad (1.17)$$

*Thermal
expansion
coefficient
and
temperature*

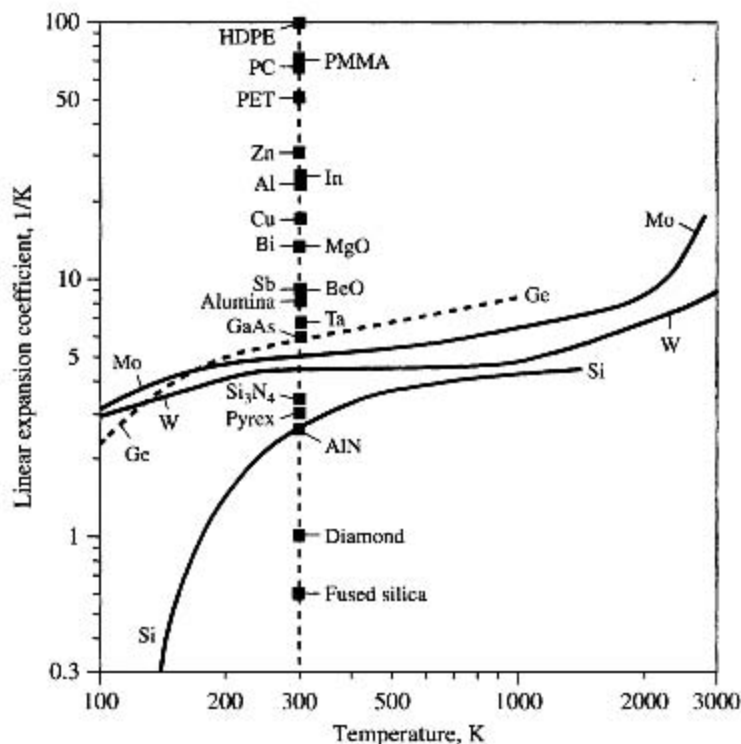


Figure 1.20 Dependence of the linear thermal expansion coefficient λ (K^{-1}) on temperature T (K) on a log-log plot.

HDPE, high-density polyethylene; PMMA, polymethylmethacrylate (acrylic); PC, polycarbonate; PET, polyethylene terephthalate (polyester); fused silica, SiO_2 ; alumina, Al_2O_3 .

SOURCE: Data extracted from various sources including G. A. Slack and S. F. Bartram, *J. Appl. Phys.*, **46**, 89, 1975.

where A , B , and C are temperature-independent constants, and the expansion is about T_0 . To find the total fractional change in the length $\Delta L/L_0$ from T_0 to T , we have to integrate $\lambda(T)$ with respect to temperature from T_0 to T . We can still employ Equation 1.15 provided that we use a properly defined mean value for the expansion coefficient from T_0 to T ,

$$L = L_0[1 + \bar{\lambda}(T - T_0)] \quad (1.18) \quad \text{Thermal expansion}$$

where
$$\bar{\lambda} = \frac{1}{(T - T_0)} \int_{T_0}^T \lambda(T) dT \quad (1.19) \quad \text{Mean thermal expansion coefficient}$$

Figure 1.20 shows the temperature dependence of λ for various materials. In very general terms, except at very low (typically below 100 K) and very high temperatures (near the melting temperature), for most metals λ does not depend strongly on the temperature; many engineers take λ for a metal to be approximately temperature independent. There is a simple relationship between the linear expansion coefficient and the heat capacity of a material, which is discussed in Chapter 4.

VOLUME EXPANSION COEFFICIENT Suppose that the volume of a solid body at temperature T_0 is V_0 . The volume expansion coefficient α_V of a solid body characterizes the change in its volume from V_0 to V due to a temperature change from T_0 to T by

$$V = V_0[1 + \alpha_V(T - T_0)] \quad (1.20) \quad \text{Volume expansion}$$

Show that α_V is given by

$$\alpha_V = 3\lambda \quad (1.21) \quad \text{Volume expansion coefficient}$$

Aluminum has a density of 2.70 g cm^{-3} at 25°C . Its thermal expansion coefficient is $24 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$. Calculate the density of Al at 350°C .

SOLUTION

Consider the solid body in the form of a rectangular parallelepiped with sides x_0 , y_0 , and z_0 . Then at T_0 ,

$$V_0 = x_0 y_0 z_0$$

and at T ,

$$\begin{aligned} V &= [x_0(1 + \lambda \Delta T)][y_0(1 + \lambda \Delta T)][z_0(1 + \lambda \Delta T)] \\ &= x_0 y_0 z_0 (1 + \lambda \Delta T)^3 \end{aligned}$$

that is

$$V = x_0 y_0 z_0 [1 + 3\lambda \Delta T + 3\lambda^2 (\Delta T)^2 + \lambda^3 (\Delta T)^3]$$

We can now substitute for V from Equation 1.20, use $V_0 = x_0 y_0 z_0$, and neglect the $\lambda^2 (\Delta T)^2$ and $\lambda^3 (\Delta T)^3$ terms compared with the $\lambda \Delta T$ term ($\lambda \ll 1$) to obtain,

$$V = V_0[1 + 3\lambda(T - T_0)] = V_0[1 + \alpha_V(T - T_0)]$$

Since density ρ is mass/volume, volume expansion leads to a density reduction. Thus,

$$\rho = \frac{\rho_0}{1 + \alpha_V(T - T_0)} \approx \rho_0[1 - \alpha_V(T - T_0)]$$

For Al, the density at 350°C is

$$\rho = 2.70[1 - 3(24 \times 10^{-6})(350 - 25)] = 2.637 \text{ g cm}^{-3}$$

EXAMPLE 1.8

EXAMPLE 1.9

Thermal
expansion
coefficient of
Si

EXPANSION OF Si The expansion coefficient of silicon over the temperature range 120–1500 K is given by Okada and Tokumaru (1984) as

$$\lambda = 3.725 \times 10^{-6} [1 - e^{-3.725 \times 10^{-3}(T-124)}] + 5.548 \times 10^{-10} T \quad (1.22)$$

where λ is in K^{-1} (or $^{\circ}\text{C}^{-1}$) and T is in kelvins. At a room temperature of 20°C , the above gives $\lambda = 2.51 \times 10^{-6} \text{K}^{-1}$. Calculate the fractional change $\Delta L/L_o$ in the length L_o of the Si crystal from 20 to 320°C , by (a) assuming a constant λ equal to the room temperature value and (b) assuming the above temperature dependence. Calculate the mean $\bar{\lambda}$ for this temperature range.

SOLUTION

Assuming a constant we have

$$\frac{\Delta L}{L_o} = \lambda(T - T_o) = (2.51 \times 10^{-6} \text{ } ^{\circ}\text{C}^{-1})(320 - 20) = 0.753 \times 10^{-3} \quad \text{or} \quad 0.075\%$$

With a temperature-dependent $\lambda(T)$,

$$\begin{aligned} \frac{\Delta L}{L_o} &= \int_{T_o}^T \lambda(T) dT \\ &= \int_{20+273}^{320+273} [3.725 \times 10^{-6} [1 - e^{-3.725 \times 10^{-3}(T-124)}] + 5.548 \times 10^{-10} T] dT \end{aligned}$$

The integration can either be done numerically or analytically (both left as an exercise) with the result that

$$\frac{\Delta L}{L_o} = 1.00 \times 10^{-3} \quad \text{or} \quad 0.1\%$$

which is substantially more than when using a constant λ . The mean $\bar{\lambda}$ over this temperature range can be found from

$$\frac{\Delta L}{L_o} = \bar{\lambda}(T - T_o) \quad \text{or} \quad 1.00 \times 10^{-3} = \bar{\lambda}(320 - 20)$$

which gives $\bar{\lambda} = 3.33 \times 10^{-6} \text{ } ^{\circ}\text{C}^{-1}$. A 0.1 percent change in length means that a 1 mm chip would expand by 1 micron.

1.5 MOLECULAR VELOCITY AND ENERGY DISTRIBUTION

Although the kinetic theory allows us to determine the root mean square velocity of the gas molecules, it says nothing about the distribution of velocities. Due to random collisions between the molecules and the walls of the container and between the molecules themselves, the molecules do not all have the same velocity. The velocity distribution of molecules can be determined experimentally by the simple scheme illustrated in Figure 1.21. Gas molecules are allowed to escape from a small aperture of a hot oven in which the substance is vaporized. Two blocking slits allow only those molecules that are moving along the line through the two slits to pass through, which results in a **collimated beam**. This beam is directed toward two rotating disks, which have slightly displaced

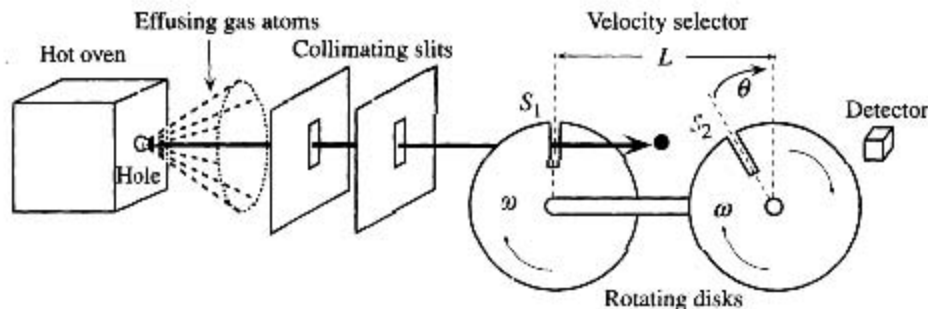


Figure 1.21 Schematic diagram of a Stern-type experiment for determining the distribution of molecular speeds.

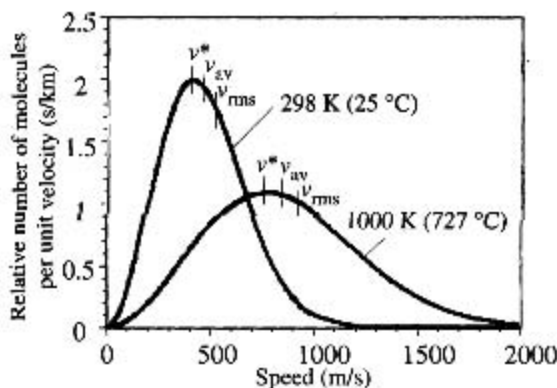


Figure 1.22 Maxwell-Boltzmann distribution of molecular speeds in nitrogen gas at two temperatures. The ordinate is $dN/(N dv)$, the fractional number of molecules per unit speed interval in $(\text{km/s})^{-1}$.

slits. The molecules that pass through the first slit can only pass through the second if they have a certain speed; that is, the exact speed at which the second slit lines up with the first slit. Thus, the two disks act as a speed selector. The speed of rotation of the disks determines which molecular speeds are allowed to go through. The experiment therefore measures the number of molecules ΔN with speeds in the range v to $(v + \Delta v)$.

It is generally convenient to describe the number of molecules dN with speeds in a certain range v to $(v + dv)$ by defining a **velocity density function** n_v as follows:

$$dN = n_v dv$$

where n_v is the number of molecules per unit velocity that have velocities in the range v to $(v + dv)$. This number represents the velocity distribution among the molecules and is a function of the molecular velocity $n_v = n_v(v)$. From the experiment, we can easily obtain n_v by $n_v = \Delta N/\Delta v$ at various velocities. Figure 1.22 shows the velocity density function n_v of nitrogen gas at two temperatures. The average (v_{av}), most probable (v^*), and rms (v_{rms}) speeds are marked to show their relative positions. As expected, these speeds all increase with increasing temperature. From various experiments of the type shown in Figure 1.21, the velocity distribution function n_v has been widely studied and found to obey the following equation:

$$n_v = 4\pi N \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2kT} \right) \quad [1.23]$$

Maxwell-Boltzmann distribution for molecular speeds

where N is the total number of molecules and m is the molecular mass. This is the **Maxwell-Boltzmann distribution function**, which describes the statistics of particle velocities in thermal equilibrium. The function assumes that the particles do not interact with each other while in motion and that all the collisions are elastic in the sense that they involve an exchange of kinetic energy. Figure 1.22 clearly shows that molecules move around randomly, with a variety of velocities ranging from nearly zero to almost infinity. The kinetic theory speaks of their rms value only.

What is the energy distribution of molecules in a gas? In the case of a monatomic gas, the total energy E is purely translational kinetic energy, so we can use $E = \frac{1}{2}mv^2$. To relate an energy range dE to a velocity range dv , we have $dE = mv dv$. Suppose that n_E is the number of atoms per unit volume per unit energy at an energy E . Then $n_E dE$ is the number of atoms with energies in the range E to $(E + dE)$. These are also the atoms with velocities in the range v to $(v + dv)$, because an atom with a velocity v has an energy E . Thus,

$$n_E dE = n_v dv$$

i.e.,

$$n_E = n_v \left(\frac{dv}{dE} \right)$$

If we substitute for n_v and (dv/dE) , we obtain the expression for n_E as a function of E :

$$n_E = \frac{2}{\pi^{1/2}} N \left(\frac{1}{kT} \right)^{3/2} E^{1/2} \exp\left(-\frac{E}{kT}\right) \quad [1.24]$$

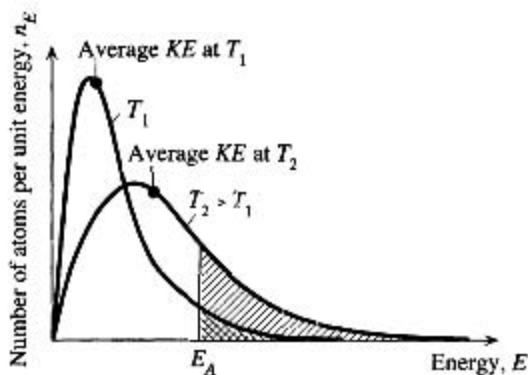
Maxwell-Boltzmann distribution for translational kinetic energies

Thus, the total internal energy is distributed among the atoms according to the Maxwell-Boltzmann distribution in Equation 1.24. The exponential factor $\exp(-E/kT)$ is called the **Boltzmann factor**. Atoms have widely differing kinetic energies, but a mean energy of $\frac{3}{2}kT$. Figure 1.23 shows the Maxwell-Boltzmann energy distribution among the gas atoms in a tank at two temperatures. As the temperature increases, the distribution extends to higher energies. The area under the curve is the total number of molecules, which remains the same for a closed container.

Equation 1.24 represents the energy distribution among the N gas atoms at any time. Since the atoms are continually colliding and exchanging energies, the energy of one

Figure 1.23 Energy distribution of gas molecules at two different temperatures.

The shaded area shows the number of molecules that have energies greater than E_A . This area depends strongly on the temperature as $\exp(-E_A/kT)$.



atom will sometimes be small and sometimes be large, but averaged over a long time, this energy will be $\frac{3}{2}kT$ as long as all the gas atoms are in thermal equilibrium (*i.e.*, the temperature is the same everywhere in the gas). Thus, we can also use Equation 1.24 to represent all possible energies an atom can acquire over a long period. There are a total of N atoms, and $n_E dE$ of them have energies in the range E to $(E + dE)$. Thus,

$$\text{Probability of energy being in } E \text{ to } (E + dE) = \frac{n_E dE}{N} \quad [1.25]$$

When the probability in Equation 1.25 is integrated (*i.e.*, summed) for all energies ($E = 0$ to ∞), the result is unity, because the atom must have an energy somewhere in the range of zero to infinity.

What happens to the Maxwell-Boltzmann energy distribution law in Equation 1.24 when the total energy is not simply translational kinetic energy? What happens when we do not have a monatomic gas? Suppose that the total energy of a molecule (which may simply be an atom) in a system of N molecules has vibrational and rotational kinetic energy contributions, as well as potential energy due to intermolecular interactions. In all cases, the number of molecules per unit energy n_E turns out to contain the Boltzmann factor, and the energy distribution obeys what is called the **Boltzmann energy distribution**:

$$\frac{n_E}{N} = C \exp\left(-\frac{E}{kT}\right) \quad [1.26]$$

*Boltzmann
energy
distribution*

where E is the total energy ($KE + PE$), N is the total number of molecules in the system, and C is a constant that relates to the specific system (*e.g.*, a monatomic gas or a liquid). The constant C may depend on the energy E , as in Equation 1.24, but not as strongly as the exponential term. Equation 1.26 is the **probability per unit energy** that a molecule in a given system has an energy E . Put differently, $(n_E dE)/N$ is the fraction of molecules in a small energy range E to $E + dE$.

MEAN AND RMS SPEEDS OF MOLECULES Given the Maxwell-Boltzmann distribution law for the velocities of molecules in a gas, derive expressions for the mean speed (v_{av}), most probable speed (v^*), and rms velocity (v_{rms}) of the molecules and calculate the corresponding values for a gas of noninteracting electrons.

EXAMPLE 1.10

SOLUTION

The number of molecules with speeds in the range v to $(v + dv)$ is

$$dN = n_v dv = 4\pi N \left(\frac{m}{2\pi kT}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2kT}\right) dv$$

By definition, then, the mean speed is given by

$$v_{av} = \frac{\int v dN}{\int dN} = \frac{\int v n_v dv}{\int n_v dv} = \sqrt{\frac{8kT}{\pi m}}$$

Mean speed

where the integration is over all speeds ($v = 0$ to ∞). The mean square velocity is given by

$$\overline{v^2} = \frac{\int v^2 dN}{\int dN} = \frac{\int v^2 n_v dv}{\int n_v dv} = \frac{3kT}{m}$$

Root mean
square
velocity

so the rms velocity is

$$v_{\text{rms}} = \sqrt{\frac{3kT}{m}}$$

where n_v/N is the probability per unit speed that a molecule has a speed in the range v to $(v + dv)$. Differentiating n_v with respect to v and setting this to zero, $dn_v/dv = 0$, gives the position of the peak of n_v versus v , and thus the most probable speed v^* ,

Most
probable
speed

$$v^* = \left[\frac{2kT}{m} \right]^{1/2}$$

Substituting $m = 9.1 \times 10^{-31}$ kg for electrons and using $T = 300$ K, we find $v^* = 95.3$ km s⁻¹, $v_{\text{av}} = 108$ km s⁻¹, and $v_{\text{rms}} = 117$ km s⁻¹, all of which are close in value. We often use the term **thermal velocity** to describe the mean speed of particles due to their thermal random motion. Also, the integrations shown are not trivial and they involve substitution and integration by parts.

1.6 HEAT, THERMAL FLUCTUATIONS, AND NOISE

Generally, thermal equilibrium between two objects implies that they have the same temperature, where temperature (from the kinetic theory) is a measure of the mean kinetic energy of the molecules. Consider a solid in a monatomic gas atmosphere such as He gas, as depicted in Figure 1.24. Both the gas and the solid are at the same temperature. The gas molecules move around randomly, with a mean kinetic energy given by $\frac{1}{2}m\overline{v^2} = \frac{3}{2}kT$, where m is the mass of the gas molecule. We also know that the atoms in the solid vibrate with a mean kinetic energy given by $\frac{1}{2}M\overline{V^2} = \frac{3}{2}kT$, where M is the mass of the solid atom and V is the velocity of vibration. The gas molecules will collide with the atoms on the surface of the solid and will thus exchange energy with those solid atoms. Since both are at the same temperature, the solid atoms and gas molecules have the same mean kinetic energy, which means that over a long time, there will be no net transfer of energy from one to the other. This is basically what we mean by **thermal equilibrium**.

If, on the other hand, the solid is hotter than the gas, $T_{\text{solid}} > T_{\text{gas}}$, and thus $\frac{1}{2}M\overline{V^2} > \frac{1}{2}m\overline{v^2}$, then when an average gas molecule and an average solid atom collide,

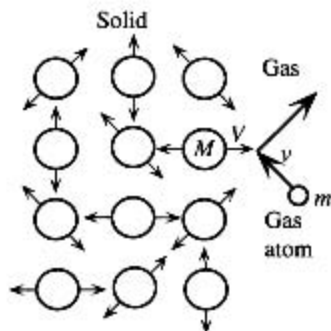


Figure 1.24 Solid in equilibrium in air.

During collisions between the gas and solid atoms, kinetic energy is exchanged.

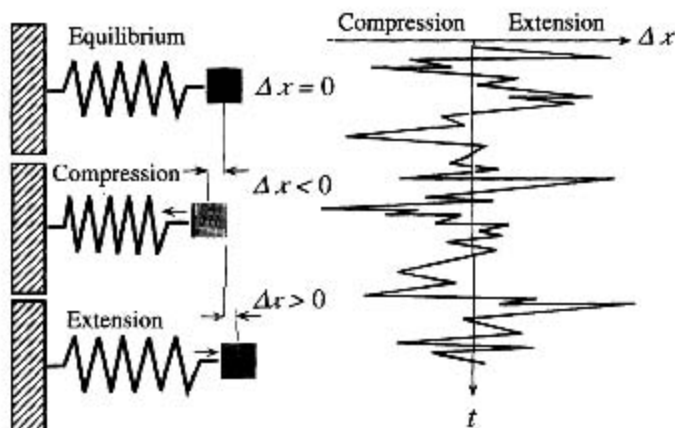


Figure 1.25 Fluctuations of a mass attached to a spring, due to random bombardment by air molecules.

energy will be transferred from the solid atom to the gas molecule. As many more gas molecules collide with solid atoms, more and more energy will be transferred, until the mean kinetic energy of atoms in each substance is the same and they reach the same temperature: the bodies have **equilibrated**. The amount of energy transferred from the kinetic energy of the atoms in the hot solid to the kinetic energy of the gas molecules is called **heat**. Heat represents the energy transfer from the hot body to the cold body by virtue of the *random* motions and collisions of the atoms and molecules.

Although, over a long time, the energy transferred between two systems in thermal equilibrium is certainly zero, this does not preclude a net energy transfer from one to the other at one instant. For example, at any one instant, an average solid atom may be hit by a fast gas molecule with a speed at the far end of the Maxwell-Boltzmann distribution. There will then be a transfer of energy from the gas molecule to the solid atom. At another instant, a slow gas molecule hits the solid, and the reverse is true. Thus, although the mean energy transferred from one atom to the other is zero, the instantaneous value of this energy is not zero and varies randomly about zero.

As an example, consider a small mass attached to a spring, as illustrated in Figure 1.25. The gas or air molecules will bombard and exchange energy with the solid atoms. Some air molecules will be fast and some will be slow, which means that there will be an instantaneous exchange of energy. Consequently, the spring will be compressed when the bombarding air molecules are fast (more energetic) and extended when they are less energetic. This leads to a mechanical fluctuation of the mass about its equilibrium position, as depicted in Figure 1.25. These fluctuations make the measurement of the exact position of the mass uncertain, and it is futile to try to measure the position more accurately than these fluctuations permit.

If the mass m compresses the spring by Δx , then at time t , the energy stored as potential energy in the spring is

$$PE(t) = \frac{1}{2} K(\Delta x)^2 \quad [1.27]$$

where K is the spring constant. At a later instant, this energy will be returned to the gas by the spring. The spring will continue to fluctuate because of the fluctuations in the velocity of the bombarding air molecules. Over a long period, the average value of PE will be the same as KE and, by virtue of the Maxwell equipartition of energy theorem, it will be given by

$$\frac{1}{2}K(\Delta x)^2 = \frac{1}{2}kT \quad [1.28]$$

Thus, the rms value of the fluctuations of the mass about its equilibrium position is

$$(\Delta x)_{rms} = \sqrt{\frac{kT}{K}} \quad [1.29]$$

To understand the origin of electrical noise, for example, we consider the thermal fluctuations in the instantaneous local electron concentration in a conductor, such as that shown in Figure 1.26. Because of fluctuations in the electron concentration at any one instant, end A of the conductor can become more negative with respect to end B, which will give rise to a voltage across the conductor. This fluctuation in the electron concentration is due to more electrons at that instant moving toward end A than toward B. At a later instant, the situation reverses and more electrons move toward B than toward A, resulting in end B becoming more negative and leading to a reversal of the voltage between A and B. Clearly, there will therefore be voltage fluctuations across the conductor, even though the mean voltage across it over a long period is always zero. If the conductor is connected to an amplifier, these voltage fluctuations will be amplified and recorded as noise at the output. This noise corrupts the actual signal at the amplifier input and is obviously undesirable. As engineers, we have to know how to calculate the magnitude of this noise. Although the mean voltage due to thermal fluctuations is zero, the rms value is not. The average voltage from a power outlet is zero, but the rms value is 120 V. We use the rms value to calculate the amount of average power available.

Consider a conductor of resistance R . To derive the noise voltage generated by R we place a capacitor C across this conductor, as in Figure 1.27, and we assume that both are at the same temperature; they are in thermal equilibrium. The capacitor is placed as a *convenient device* to obtain or derive the noise voltage generated by R . It should be emphasized that C itself does not contribute to the source of the fluctuations (it generates no noise) but is inserted into the circuit to impose a finite *bandwidth* over which we will calculate the noise voltage. The reason is that all practical electric circuits have some kind of bandwidth, and the noise voltage we will derive depends on this bandwidth. Even if we remove the capacitor, there will still be stray capacitances; and if we short the conductor, the shorting wires will have some inductance that will also impose a bandwidth. As we mentioned previously, thermal fluctuations in the conductor give rise to voltage fluctuations across R . There is only so much average energy available in these thermal fluctuations, and this is the energy that is used to charge and discharge the external capacitor C . The voltage across the capacitor depends on how much energy that can be stored on it, which in turn depends on the thermal fluctuations in the conductor. Charging a capacitor to a voltage v implies that an energy $E = \frac{1}{2}Cv^2$ is stored on the capacitor. The mean stored energy \bar{E} in a thermal equilibrium system can only be

Root mean
square
fluctuations
of a body
attached to a
spring of
stiffness K

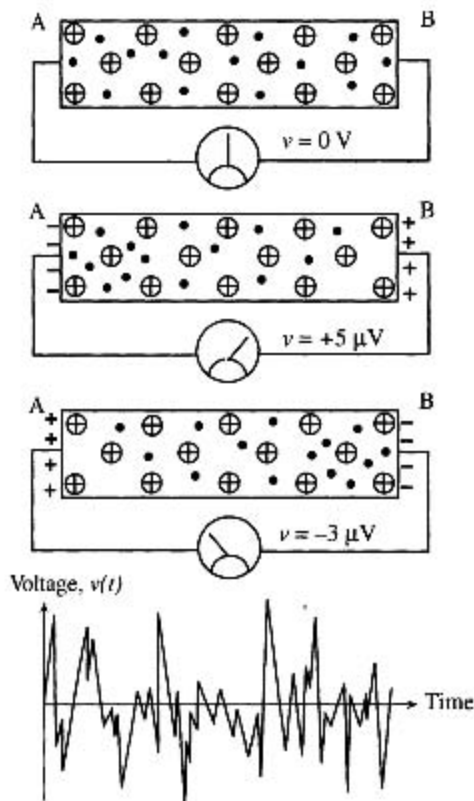


Figure 1.26 Random motion of conduction electrons in a conductor, resulting in electrical noise.

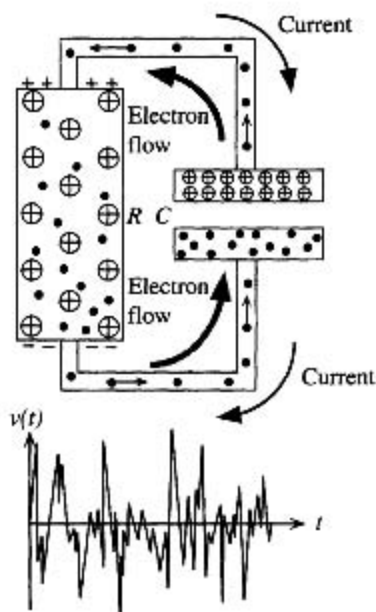


Figure 1.27 Charging and discharging of a capacitor by a conductor, due to the random thermal motions of the conduction electrons.

$\frac{1}{2}kT$, according to the Maxwell energy equipartition theorem. Thus $\overline{E(t)}$, the mean energy stored on C due to thermal fluctuations, is given by

$$\overline{E(t)} = \frac{1}{2}C\overline{v(t)^2} = \frac{1}{2}kT$$

We see that the mean square voltage across the capacitor is given by

$$\overline{v(t)^2} = \frac{kT}{C} \quad [1.30]$$

Interestingly, the rms noise voltage across an RC network seems to be independent of the resistance. However, the origin of the noise voltage arises from the electron fluctuations in the conductor and we must somehow reexpress Equation 1.30 to reflect this fact; that is, we must relate the electrical fluctuations to R .

The voltage fluctuations across the network will have many sinusoidal components, but only those below the cutoff frequency of the RC network will contribute to the mean

square voltage (that is, we effectively have a low-pass filter). If B is the bandwidth of the RC network,⁸ then $B = 1/(2\pi RC)$ and we can eliminate C in Equation 1.30 to obtain

$$\overline{v(t)^2} = 2\pi kTRB$$

This is the key equation for calculating the mean square noise voltage from a resistor over a bandwidth B . A more rigorous derivation makes the numerical factor 4 rather than 2π . For a network with a bandwidth B , the **rms noise voltage** is therefore

$$v_{\text{rms}} = \sqrt{4kTRB} \quad [1.31]$$

Root mean
square noise
voltage
across a
resistance

Equation 1.31 is known as the **Johnson resistor noise equation**, and it sets the lower limit of the magnitude of small signals that can be amplified. Note that Equation 1.31 basically tells us the rms value of the voltage fluctuations within a given bandwidth (B) and not the origin and spectrum (noise voltage vs. frequency) of the noise. The origin of noise is attributed to the random motions of electrons in the conductor (resistor), and Equation 1.31 is the fundamental description of electrical fluctuations; that is, the fluctuations in the conductor's instantaneous local electron concentration that charges and discharges the capacitor. To determine the rms noise voltage across a network with an impedance $Z(j\omega)$, all we have to do is find the real part of Z , which represents the resistive part, and use this for R in Equation 1.31.

EXAMPLE 1.11

NOISE IN AN RLC CIRCUIT Most radio receivers have a tuned parallel-resonant circuit, which consists of an inductor L , capacitor C , and resistance R in parallel. Suppose L is $100 \mu\text{H}$; C is 100 pF ; and R , the equivalent resistance due to the input resistance of the amplifier and to the loss in the coil (coil resistance plus ferrite losses), is about $200 \text{ k}\Omega$. What is the minimum rms radio signal that can be detected?

SOLUTION

Consider the bandwidth of this tuned RLC circuit, which can be found in any electrical engineering textbook:

$$B = \frac{f_o}{Q}$$

where $f_o = 1/[2\pi\sqrt{LC}]$ is the resonant frequency and $Q = 2\pi f_o CR$ is the quality factor. Substituting for L , C , and R , we get, $f_o = 10^7/2\pi = 1.6 \times 10^6 \text{ Hz}$ and $Q = 200$, which gives $B = 10^7/[2\pi(200)] \text{ Hz}$, or 8 kHz . The rms noise voltage is

$$\begin{aligned} v_{\text{rms}} &= [4kTRB]^{1/2} = [4(1.38 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K})(200 \times 10^3 \Omega)(8 \times 10^3 \text{ Hz})]^{1/2} \\ &= 5.1 \times 10^{-6} \text{ V} \quad \text{or} \quad 5.1 \mu\text{V} \end{aligned}$$

This rms voltage is within a bandwidth of 8 kHz centered at 1.6 MHz . This last information is totally absent in Equation 1.31. If we attempt to use

$$v_{\text{rms}} = \left[\frac{kT}{C} \right]^{1/2}$$

⁸ A low-pass filter allows all signal frequencies up to the cutoff frequency B to pass. B is $1/(2\pi RC)$.

we get

$$v_{\text{rms}} = \left[\frac{(1.38 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K})}{100 \times 10^{-12} \text{ F}} \right]^{1/2} = 6.4 \mu\text{V}$$

However, Equation 1.30 was derived using the RC circuit in Figure 1.27, whereas we now have an LCR circuit. The correct approach uses Equation 1.31, which is generally valid, and the appropriate bandwidth B .

1.7 THERMALLY ACTIVATED PROCESSES

1.7.1 ARRHENIUS RATE EQUATION

Many physical and chemical processes strongly depend on temperature and exhibit what is called an **Arrhenius type behavior**, in which the rate of change is proportional to $\exp(-E_A/kT)$, where E_A is a characteristic energy parameter applicable to the particular process. For example, when we store food in the refrigerator, we are effectively using the Arrhenius rate equation: cooling the food diminishes the rate of decay. Processes that exhibit an Arrhenius type temperature dependence are referred to as **thermally activated**.

For an intuitive understanding of a thermally activated process, consider a vertical filing cabinet that stands in equilibrium, with its center of mass at A , as sketched in Figure 1.28. Tilting the cabinet left or right increases the potential energy PE and requires external work. If we could supply this energy, we could move the cabinet over its edge and lay it flat, where its PE would be lower than at A . Clearly, since the PE at B is lower, this is a more stable position than A . Further, in going from A to B , we had to overcome a **potential energy barrier** of amount E_A , which corresponds to the cabinet standing on its edge with the center of mass at the highest point at A^* . To topple the cabinet, we must first provide energy⁹ equal to E_A to take the center of mass to A^* , from which point the cabinet, with the slightest encouragement, will fall spontaneously to B to attain the lowest PE . At the end of the whole tilting process, the internal energy change for the cabinet, ΔU , is due to the change in the $PE (= mgh)$ from A to B , which is negative; B has lower PE than A .

Suppose, for example, a person with an average energy less than E_A tries to topple the cabinet. Like everyone else, that person experiences energy fluctuations as a result of interactions with the environment (e.g., what type of day the person had). During one of those high-energy periods, he can topple the cabinet, even though most of the time he cannot do so because his average energy is less than E_A . The rate at which the cabinet is toppled depends on the number of times (frequency) the person tries and the probability that he possesses energy greater than E_A .

As an example of a thermally activated process, consider the diffusion of impurity atoms in a solid, one of which is depicted in Figure 1.29. In this example, the impurity atom is at an interatomic void A in the crystal, called an **interstitial site**. For the impurity atom to move from A to a neighboring void B , the atom must push the host neighbors apart as it moves across. This requires energy in much the same way

⁹ According to the conservation of energy principle, the increase in the PE from A to A^* must come from the external work.

Figure 1.28 Tilting a filing cabinet from state A to its edge in state A* requires an energy E_A .

After reaching A*, the cabinet spontaneously drops to the stable position B. The PE of state B is lower than A, and therefore state B is more stable than A.

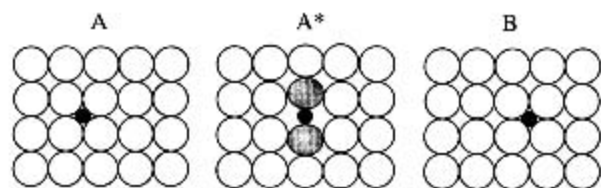
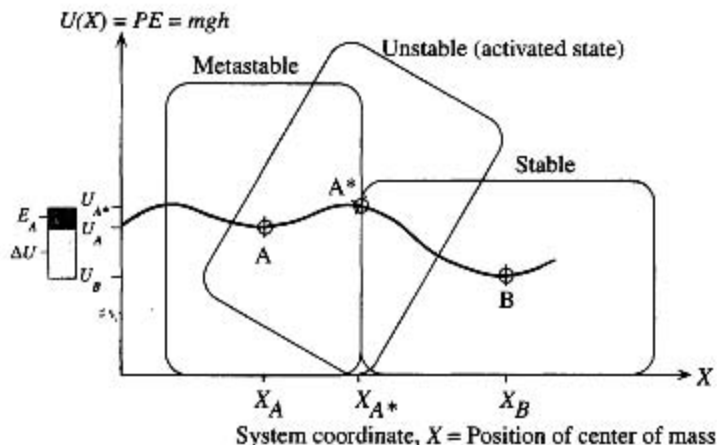
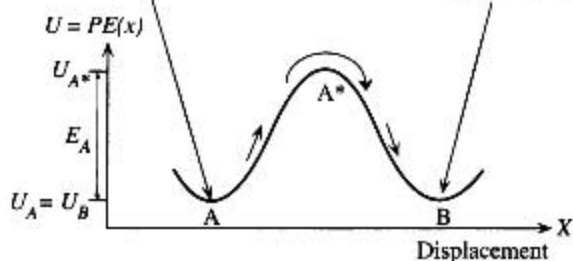


Figure 1.29 Diffusion of an interstitial impurity atom in a crystal from one void to a neighboring void.

The impurity atom at position A must possess an energy E_A to push the host atoms away and move into the neighboring void at B.



as does toppling the filing cabinet. There is a potential energy barrier E_A to the motion of this atom from A to B.

Both the host and the impurity atoms in the solid vibrate about their equilibrium positions, with a distribution of energies, and they also continually exchange energies, which leads to energy fluctuations. In thermal equilibrium, at any instant, we can expect the energy distribution of the atoms to obey the Boltzmann distribution law (see Equation 1.26). The average kinetic energy per atom is vibrational and is $\frac{3}{2}kT$, which will not allow the impurity simply to overcome the PE barrier E_A , because typically $E_A \gg \frac{3}{2}kT$.

The rate of jump, called the **diffusion**, of the impurity from A to B depends on two factors. The first is the number of times the atom tries to go over the potential barrier, which is the vibrational frequency ν_0 , in the AB direction. The second factor is the probability that the atom has sufficient energy to overcome the PE barrier. Only during those times when the atom has an energy greater than the potential energy barrier $E_A = U_{A^*} - U_A$ will it jump across from A to B. During this diffusion process, the atom attains an **activated state**, labeled A* in Figure 1.29, with an energy E_A above U_A , so the crystal internal energy is higher than U_A . E_A is called the **activation energy**.

Suppose there are N impurity atoms. At any instant, according to the Boltzmann distribution, $n_E dE$ of these will have kinetic energies in the range E to $(E + dE)$, so the probability that an impurity atom has an energy E greater than E_A is

$$\begin{aligned} \text{Probability } (E > E_A) &= \frac{\text{Number of impurities with } E > E_A}{\text{Total number of impurities}} \\ &= \frac{\int_{E_A}^{\infty} n_E dE}{N} = A \exp\left(-\frac{E_A}{kT}\right) \end{aligned}$$

where A is a dimensionless constant that has only a weak temperature dependence. The rate of jumps, jumps per seconds, or simply the **frequency of jumps** ϑ from void to void is

$$\begin{aligned} \vartheta &= (\text{Frequency of attempt along AB})(\text{Probability of } E > E_A) \\ &= A v_a \exp\left(-\frac{E_A}{kT}\right) \quad E_A = U_{A*} - U_A \end{aligned} \quad [1.32]$$

Rate for a thermally activated process

Equation 1.32 describes the rate of a thermally activated process, for which increasing the temperature causes more atoms to be energetic and hence results in more jumps over the potential barrier. Equation 1.32 is the well-known **Arrhenius rate equation** and is generally valid for a vast number of transformations, both chemical and physical.

1.7.2 ATOMIC DIFFUSION AND THE DIFFUSION COEFFICIENT

Consider the motion of the impurity atom in Figure 1.29. For simplicity, assume a two-dimensional crystal in the plane of the paper, as in Figure 1.30. The impurity atom has four neighboring voids into which it can jump. If θ is the angle with respect to the x axis, then these voids are at directions $\theta = 0^\circ, 90^\circ, 180^\circ,$ and 270° ; as depicted in Figure 1.30. Each jump is in a random direction along one of these four angles. As the impurity atom jumps from void to void, it leaves its original location at O , and after N jumps, after time t , it has been displaced from O to O' .

Let a be the closest void-to-void separation. Each jump results in a displacement along x which is equal to $a \cos \theta$, with $\theta = 0^\circ, 90^\circ, 180^\circ,$ or 270° . Thus, each jump

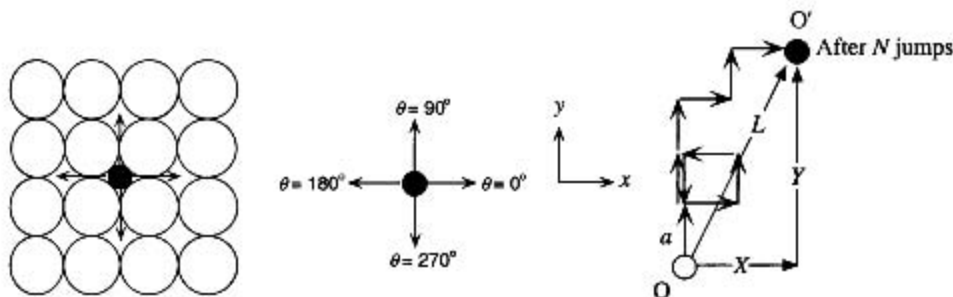


Figure 1.30 An impurity atom has four site choices for diffusion to a neighboring interstitial vacancy. After N jumps, the impurity atom would have been displaced from the original position at O .

results in a displacement along x which can be a , 0 , $-a$, or 0 , corresponding to the four possibilities. After N jumps, the mean displacement along x will be close to zero, just as the mean voltage of the ac voltage from a power outlet is zero, even though it has an rms value of 120 V. We therefore consider the square of the displacements. The total square displacement, denoted X^2 , is

$$X^2 = a^2 \cos^2 \theta_1 + a^2 \cos^2 \theta_2 + \dots + a^2 \cos^2 \theta_N$$

Clearly, $\theta = 90^\circ$ and 270° give $\cos^2 \theta = 0$. Of all N jumps, $\frac{1}{2}N$ are $\theta = 0$ and 180° , each of which gives $\cos^2 \theta = 1$. Thus,

$$X^2 = \frac{1}{2}a^2N$$

There will be a similar expression for Y^2 , which means that after N jumps, the total square distance L^2 from O to O' in Figure 1.30 is

$$L^2 = X^2 + Y^2 = a^2N$$

The rate of jumping (frequency of jumps) is given by Equation 1.32

$$\vartheta = v_o A \exp\left(-\frac{E_A}{kT}\right)$$

so the time per jump is $1/\vartheta$. Time t for N jumps is N/ϑ . Thus, $N = \vartheta t$ and

$$L^2 = a^2 \vartheta t = 2Dt \quad [1.33]$$

where, by definition, $D = \frac{1}{2}a^2\vartheta$, which is a constant that depends on the diffusion process, as well as the temperature, by virtue of ϑ . This constant is generally called the **diffusion coefficient**. Substituting for ϑ , we find

$$D = \frac{1}{2}a^2 v_o A \exp\left(-\frac{E_A}{kT}\right)$$

or

$$D = D_o \exp\left(-\frac{E_A}{kT}\right) \quad [1.34]$$

where D_o is a constant. The root square displacement L in time t , from Equation 1.33, is given by $L = [2Dt]^{1/2}$. Since L^2 is evaluated from X^2 and Y^2 , L is known as the **root mean square (rms) displacement**.

The preceding specific example considered the diffusion of an impurity in a void between atoms in a crystal; this is a simple way to visualize the diffusion process. An impurity, indeed any atom, at a regular atomic site in the crystal can also diffuse around by various other mechanisms. For example, such an impurity can simultaneously exchange places with a neighbor. But, more significantly, if a neighboring atomic site has a *vacancy* that has been left by a missing host atom, then the impurity can simply jump into this vacancy. (Vacancies in crystals are explained in detail in Section 1.9.1; for the present, they simply correspond to missing atoms in the crystal.) The activation energy E_A in Equation 1.34 is a measure of the difficulty of the diffusion process. It may be as simple as the energy (or work) required for an impurity atom to deform (or strain) the crystal around it as it jumps from one interstitial site to a neighboring interstitial site, as in Figure 1.29; or it may be more complicated, for example, involving vacancy creation.

Mean square
displacement

Diffusion
coefficient

Various Si semiconductor devices are fabricated by doping a single Si crystal with impurities (dopants) at high temperatures. For example, doping the Si crystal with phosphorus (P) gives the crystal a higher electrical conductivity. The P atoms substitute directly for Si atoms in the crystal. These dopants migrate from high to low dopant concentration regions in the crystal by diffusion, which occurs efficiently only at sufficiently high temperatures.

DIFFUSION OF DOPANTS IN SILICON The diffusion coefficient of P atoms in the Si crystal follows Equation 1.34 with $D_0 = 10.5 \text{ cm}^2 \text{ s}^{-1}$ and $E_A = 3.69 \text{ eV}$. What is the diffusion coefficient at a temperature of 1100°C at which dopants such as P are diffused into Si to fabricate various devices? What is the rms distance diffused by P atoms in 5 minutes? Estimate, as an order of magnitude, how many jumps the P atom makes in 1 second if you take the jump distance to be roughly the mean interatomic separation, $\sim 0.27 \text{ nm}$.

EXAMPLE 1.12**SOLUTION**

From Equation 1.34,

$$D = D_0 \exp\left(-\frac{E_A}{kT}\right) = (10.5 \text{ cm}^2 \text{ s}^{-1}) \exp\left[-\frac{(3.69 \text{ eV})(1.602 \times 10^{-19} \text{ J eV}^{-1})}{(1.381 \times 10^{-23} \text{ J K}^{-1})(1100 + 273 \text{ K})}\right]$$

$$= 3.0 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$$

The rms distance L diffused in a time $t = 5 \text{ min} = 5 \times 60 \text{ seconds}$ is

$$L = \sqrt{2Dt} = [2(3.0 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1})(5 \times 60 \text{ s})]^{1/2} = 1.3 \times 10^{-5} \text{ cm} \quad \text{or} \quad 13 \mu\text{m}$$

Equation 1.33 was derived for a two-dimensional crystal as in Figure 1.30, and for an impurity diffusion. Nonetheless, we can still use it to estimate how many jumps a P atom makes in 1 second. From Equation 1.33, $\bar{\nu} \approx 2D/a^2 \approx 2(3.0 \times 10^{-13} \text{ m}^2 \text{ s}^{-1})/(0.27 \times 10^{-9} \text{ m})^2 = 823$ jumps per second. It takes roughly 1 ms to make one jump. It is left as an exercise to show that at room temperature it will take a P atom 10^{46} years to make a jump! (Scientists and engineers know how to use thermally activated processes.)

1.8 THE CRYSTALLINE STATE

1.8.1 TYPES OF CRYSTALS

A **crystalline solid** is a solid in which the atoms bond with each other in a regular pattern to form a periodic collection (or array) of atoms, as shown for the copper crystal in Figure 1.31. The most important property of a crystal is **periodicity**, which leads to what is termed **long-range order**. In a crystal, the local bonding geometry is repeated many times at regular intervals, to produce a periodic array of atoms that constitutes the crystal structure. The location of each atom is well known by virtue of periodicity. There is therefore a long-range order, since we can always predict the atomic arrangement anywhere in the crystal. Nearly all metals, many ceramics and semiconductors, and various polymers are crystalline solids in the sense that the atoms or molecules are positioned on a **periodic array of points in space**.

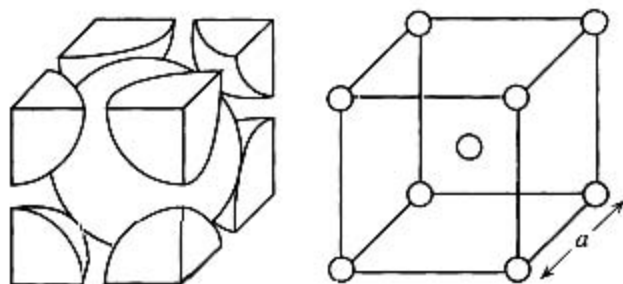


Figure 1.32 Body-centered cubic (BCC) crystal structure.

(a) A BCC unit cell with close-packed hard spheres representing the Fe atoms.

(b) A reduced-sphere unit cell.

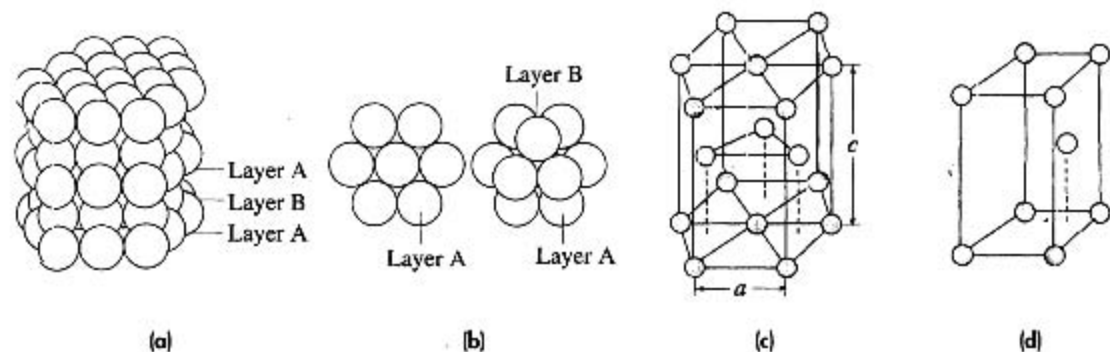


Figure 1.33 The hexagonal close-packed (HCP) crystal structure.

(a) The hexagonal close-packed (HCP) structure. A collection of many Zn atoms. Color difference distinguishes layers (stacks).

(b) The stacking sequence of closely packed layers is ABAB.

(c) A unit cell with reduced spheres.

(d) The smallest unit cell with reduced spheres.

Assuming the Cu atoms are spheres that touch each other, we can geometrically relate a and R . For clarity, it is often more convenient to draw the unit cell with the spheres reduced, as in Figure 1.31c.

The FCC crystal structure of Cu is known as a **close-packed crystal structure** because the Cu atoms are packed as closely as possible, as is apparent in Figure 1.31a and b. The volume of the FCC unit cell is 74 percent full of atoms, which is the maximum packing possible with identical spheres. By comparison, iron has a **body-centered cubic (BCC)** crystal structure and its unit cell is shown in Figure 1.32. The BCC unit cell has Fe atoms at its corners and one Fe atom at the center of the cell. The volume of the BCC unit cell is 68 percent full of atoms, which is lower than the maximum possible packing.

The FCC crystal structure is only one way to pack the atoms as closely as possible. For example, in zinc, the atoms are arranged as closely as possible in a hexagonal symmetry, to form the **hexagonal close-packed (HCP) structure** shown in Figure 1.33a. This structure corresponds to packing spheres as closely as possible first as one layer A, as shown in Figure 1.33b. You can visualize this by arranging six pennies as closely as possible on a table top. On top of layer A we can place an identical layer B, with the

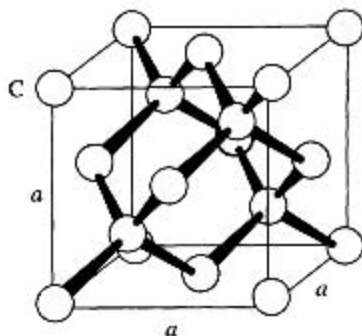


Figure 1.34 The diamond unit cell which is cubic. The cell has eight atoms.

Gray Sn (α -Sn) and the elemental semiconductors Ge and Si have this crystal structure.

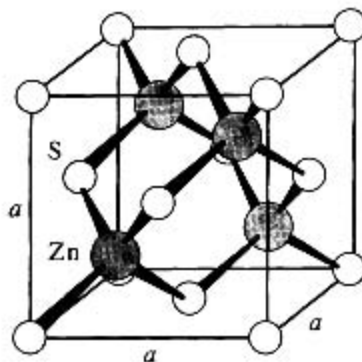


Figure 1.35 The zinc blende (ZnS) cubic crystal structure.

Many important compound crystals have the zinc blende structure. Examples: AlAs, GaAs, GaP, GaSb, InAs, InP, InSb, ZnS, ZnTe.

spheres taking up the voids on layer A, as depicted in Figure 1.33b. The third layer can be placed on top of B and lined up with layer A. The stacking sequence is therefore ABAB. . . . A unit cell for the HCP structure is shown in Figure 1.33c, which shows that this is not a cubic structure. The unit cell shown, although convenient, is not the smallest unit cell. The smallest unit cell for the HCP structure is shown in Figure 1.33d and is called the **hexagonal unit cell**. The repetition of this unit cell will generate the whole HCP structure. The atomic packing density in the HCP crystal structure is 74 percent, which is the same as that in the FCC structure.

Covalently bonded solids, such as silicon and germanium, have a diamond crystal structure brought about by the directional nature of the covalent bond, as shown in Figure 1.34 (see also Figure 1.6). The rigid local bonding geometry of four Si-Si bonds in the tetrahedral configuration forces the atoms to form what is called the **diamond cubic crystal structure**. The unit cell in this case can be identified with the cubic structure. Although there are atoms at each corner and at the center of each face, indicating an FCC-like structure, there are four atoms within the cell as well. Thus, there are eight atoms in the unit cell. The diamond unit cell can actually be described in terms of an FCC lattice (a geometric arrangement of points) with each lattice point having a basis of two Si atoms. If we place the two Si atoms at each site appropriately, for example, one right at the lattice point, and the other displaced from it by a quarter lattice distance $a/4$ along the cube edges, we can easily generate the diamond unit cell. In the copper crystal, each FCC lattice point has one Cu atom, whereas in the Si crystal each lattice point has two Si atoms; thus there are $4 \times 2 = 8$ atoms in the diamond unit cell.

In the GaAs crystal, as in the silicon crystal, each atom forms four directional bonds with its neighbors. The unit cell looks like a diamond cubic, as indicated in Figure 1.35 but with the Ga and As atoms alternating positions. This unit cell is termed

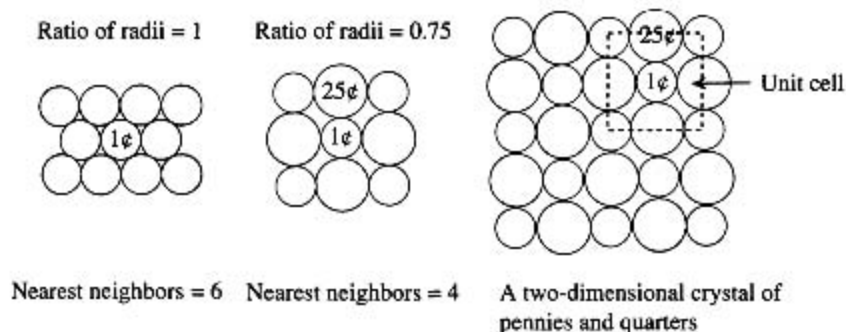


Figure 1.36 Packing of coins on a table top to build a two-dimensional crystal.

the **zinc blende** structure after ZnS , which has this type of unit cell. Many important compound semiconductors have this crystal structure, GaAs being the most commonly known. The zinc blende unit cell can also be described in terms of a fundamental FCC lattice and a basis that has two atoms, Zn and S (or Ga and As). For example, we can place one Zn at each lattice point and one S atom displaced from the Zn by $a/4$ along the cube edges.

In ionic solids, the cations (e.g., Na^+) and the anions (Cl^-) attract each other nondirectionally. The crystal structure depends on how closely the opposite ions can be brought together and how the same ions can best avoid each other while maintaining long-range order, or maintaining symmetry. These depend on the relative charge and relative size per ion.

To demonstrate the importance of the size effect in two dimensions, consider identical coins, say pennies (1-cent coins). At most, we can make six pennies touch one penny, as shown in Figure 1.36. On the other hand, if we use quarters¹¹ (25-cent coins) to touch one penny, at most only five quarters can do so. However, this arrangement cannot be extended to the construction of a two-dimensional crystal with periodicity. To fulfill the long-range symmetry requirement for crystals, we can only use four quarters to touch the penny and thereby build a two-dimensional “penny–quarter” crystal, which is shown in the figure. In the two-dimensional crystal, a penny has four quarters as nearest neighbors; similarly, a quarter has four pennies as nearest neighbors. A convenient unit cell is a square cell with one-quarter of a penny at each corner and a full penny at the center (as shown in the figure).

The three-dimensional equivalent of the unit cell of the penny–quarter crystal is the **NaCl unit cell** shown in Figure 1.37. The Na^+ ion is about half the size of the Cl^- ion, which permits six nearest neighbors while maintaining long-range order. The repetition of this unit cell in three dimensions generates the whole NaCl crystal, which was depicted in Figure 1.9b.

A similar unit cell with Na^+ and Cl^- interchanged is also possible and equally convenient. We can therefore describe the whole crystal with two interpenetrating FCC

¹¹ Although many are familiar with the United States coinage, any two coins with a size ratio of about 0.75 would work out the same.

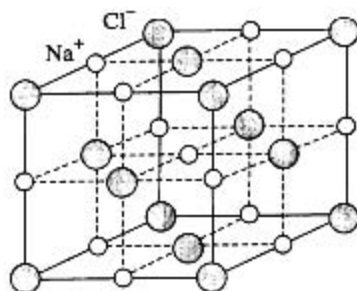


Figure 1.37 A possible reduced-sphere unit cell for the NaCl (rock salt) crystal.

An alternative unit cell may have Na⁺ and Cl⁻ interchanged. Examples: AgCl, CaO, CsF, LiF, LiCl, NaF, NaCl, KF, KCl, MgO.

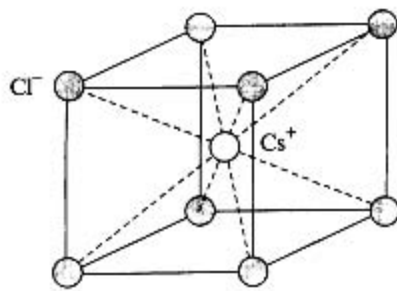


Figure 1.38 A possible reduced-sphere unit cell for the CsCl crystal.

An alternative unit cell may have Cs⁺ and Cl⁻ interchanged. Examples: CsCl, CsBr, CsI, TlCl, TlBr, TlI.

unit cells, each having oppositely charged ions at the corners and face centers. Many ionic solids have the rock salt (NaCl) crystal structure.

When the cation and anions have equal charges and are about the same size, as in the CsCl crystal, the unit cell is called the **CsCl structure**, which is shown in Figure 1.38. Each cation is surrounded by eight anions (and vice versa), which are at

Table 1.3 Properties of some important crystal structures

Crystal Structure	a and R (R is the Radius of the Atom)	Coordination Number (CN)	Number of Atoms per Unit Cell	Atomic Packing Factor	Examples
Simple cubic	$a = 2R$	6	1	0.52	No metals (Except Po)
BCC	$a = \frac{4R}{\sqrt{3}}$	8	2	0.68	Many metals: α -Fe, Cr, Mo, W
FCC	$a = \frac{4R}{\sqrt{2}}$	12	4	0.74	Many metals: Ag, Au, Cu, Pt
HCP	$a = 2R$ $c = 1.633a$	12	2	0.74	Many metals: Co, Mg, Ti, Zn
Diamond	$a = \frac{8R}{\sqrt{3}}$	4	8	0.34	Covalent solids: Diamond, Ge, Si, α -Sn
Zinc blende		4	8	0.34	Many covalent and ionic solids. Many compound semiconductors. ZnS, GaAs, GaSb, InAs, InSb
NaCl		6	4 cations 4 anions	0.67 (NaCl)	Ionic solids such as NaCl, AgCl, LiF, MgO, CaO Ionic packing factor depends on relative sizes of ions.
CsCl		8	1 cation 1 anion		Ionic solids such as CsCl, CsBr, CsI

the corners of a cube. This is not a true BCC unit cell because the atoms at various BCC lattice points are different. (As discussed in Section 1.13, CsCl has a simple cubic lattice with a basis that has one Cl^- ion and one Na^+ ion.)

Table 1.3 summarizes some of the important properties of the main crystal structures considered in this section.

THE COPPER (FCC) CRYSTAL Consider the FCC unit cell of the copper crystal shown in Figure 1.39.

EXAMPLE 1.13

- How many atoms are there per unit cell?
- If R is the radius of the Cu atom, show that the lattice parameter a is given by $a = R2\sqrt{2}$.
- Calculate the **atomic packing factor** (APF) defined by

$$\text{APF} = \frac{\text{Volume of atoms in unit cell}}{\text{Volume of unit cell}}$$

- Calculate the **atomic concentration** (number of atoms per unit volume) in Cu and the density of the crystal given that the atomic mass of Cu is 63.55 g mol^{-1} and the radius of the Cu atom is 0.128 nm .

SOLUTION

- There are four atoms per unit cell. The Cu atom at each corner is shared with eight other adjoining unit cells. Each Cu atom at the face center is shared with the neighboring unit cell. Thus, the number of atoms in the unit cell = 8 corners ($\frac{1}{8}$ atom) + 6 faces ($\frac{1}{2}$ atoms) = 4 atoms.
- Consider the unit cell shown in Figure 1.39 and one of the cubic faces. The face is a square of side a and the diagonal is $\sqrt{a^2 + a^2}$ or $a\sqrt{2}$. The diagonal has one atom at the center of diameter $2R$, which touches two atoms centered at the corners. The diagonal, going from corner to corner, is therefore $R + 2R + R$. Thus, $4R = a\sqrt{2}$ and $a = 4R/\sqrt{2} = R2\sqrt{2}$. Therefore, $a = 0.3620 \text{ nm}$.

- $\text{APF} = \frac{(\text{Number of atoms in unit cell}) \times (\text{Volume of atom})}{\text{Volume of unit cell}}$

$$= \frac{4 \times \frac{4}{3}\pi R^3}{a^3} = \frac{\frac{4^2}{3}\pi R^3}{(R2\sqrt{2})^3} = \frac{4^2\pi}{3(2\sqrt{2})^3} = 0.74$$

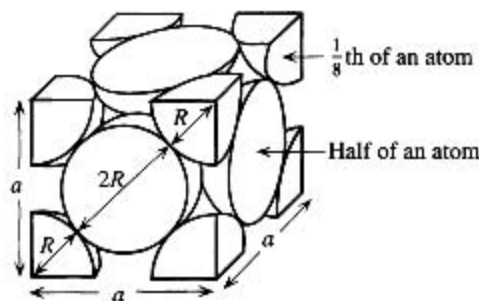


Figure 1.39 The FCC unit cell. The atomic radius is R and the lattice parameter is a .

d. In general, if there are x atoms in the unit cell, the atomic concentration is

$$n_{\text{at}} = \frac{\text{Number of atoms in unit cell}}{\text{Volume of unit cell}} = \frac{x}{a^3}$$

Thus, for Cu

$$n_{\text{at}} = \frac{4}{(0.3620 \times 10^{-7} \text{ cm})^3} = 8.43 \times 10^{22} \text{ cm}^{-3}$$

There are x atoms in the unit cell, and each atom has a mass of M_{at}/N_A grams. The density ρ is

$$\rho = \frac{\text{Mass of all atoms in unit cell}}{\text{Volume of unit cell}} = \frac{x \left(\frac{M_{\text{at}}}{N_A} \right)}{a^3}$$

that is,
$$\rho = \frac{n_{\text{at}} M_{\text{at}}}{N_A} = \frac{(8.43 \times 10^{22} \text{ cm}^{-3})(63.55 \text{ g mol}^{-1})}{6.022 \times 10^{23} \text{ mol}^{-1}} = 8.9 \text{ g cm}^{-3}$$

The expression $\rho = (n_{\text{at}} M_{\text{at}})/N_A$ is independent of the crystal structure.

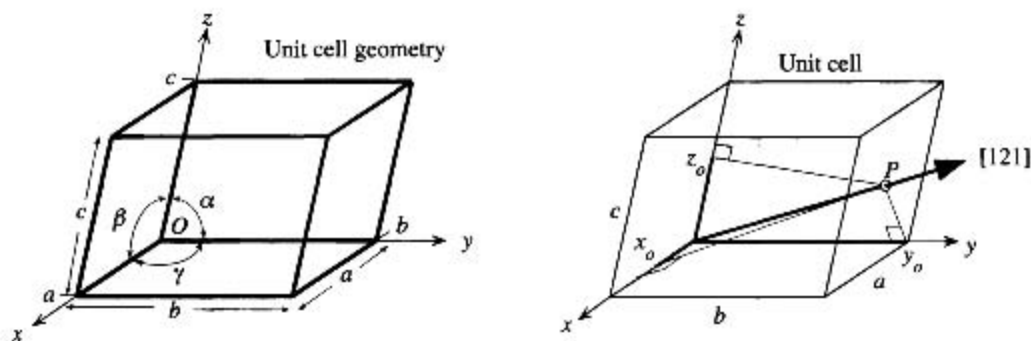
1.8.2 CRYSTAL DIRECTIONS AND PLANES

There can be a number of possibilities for choosing a unit cell for a given crystal structure, as is apparent in Figure 1.33c and d for the HCP crystal. As a convention, we generally represent the **geometry of the unit cell** as a parallelepiped with sides a , b , and c and angles α , β , and γ , as depicted in Figure 1.40a. The sides a , b , and c and angles α , β , and γ are referred to as the **lattice parameters**. To establish a reference frame and to apply three-dimensional geometry, we insert an xyz coordinate system. The x , y , and z axes follow the edges of the parallelepiped and the origin is at the lower-left rear corner of the cell. The unit cell extends along the x axis from 0 to a , along y from 0 to b , and along z from 0 to c .

For Cu and Fe, the unit-cell geometry has $a = b = c$, $\alpha = \beta = \gamma = 90^\circ$, and cubic symmetry. For Zn, the unit cell has hexagonal geometry, with $a = b \neq c$, $\alpha = \beta = 90^\circ$, and $\gamma = 120^\circ$, as shown in Figure 1.33d.

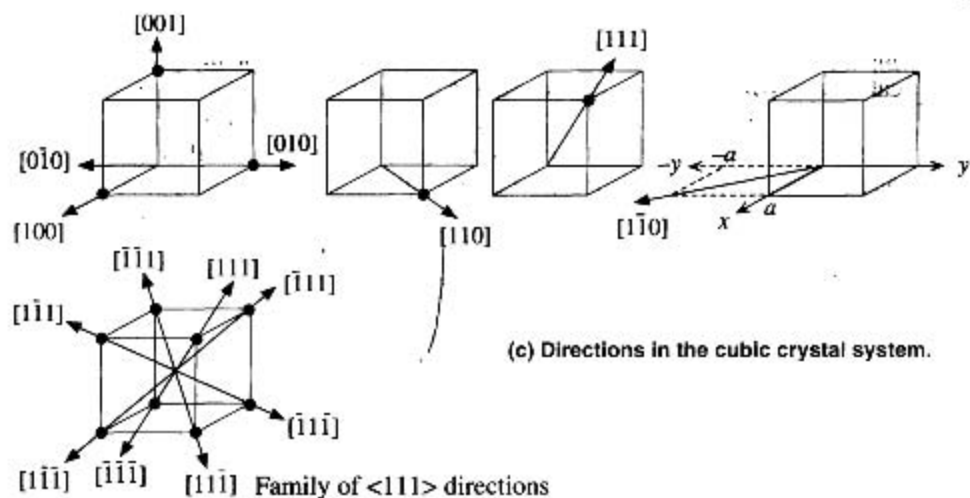
In explaining crystal properties, we must frequently specify a direction in a crystal, or a particular plane of atoms. Many properties, for example, the elastic modulus, electrical resistivity, magnetic susceptibility, etc., are directional within the crystal. We use the convention described here for labeling crystal directions based on three-dimensional geometry.

All parallel vectors have the same indices. Therefore, the direction to be labeled can be moved to pass through the origin of the unit cell. As an example, Figure 1.40b shows a direction whose indices are to be determined. A point P on the vector can be expressed by the coordinates x_o , y_o , z_o , where x_o , y_o , and z_o are projections from point P onto the x , y , and z axes, respectively, as shown in Figure 1.40b. It is generally convenient to place P where the line cuts a surface (though this is not necessary). We can express these coordinates in terms of the lattice parameters a , b , and c , respectively. We then have three coordinates, say x_1 , y_1 , and z_1 , for point P in terms of a , b , and c .



(a) A parallelepiped is chosen to describe the *geometry* of a unit cell. We line the *x*, *y*, and *z* axes with the edges of the parallelepiped taking the lower-left rear corner as the origin.

(b) Identification of a direction in a crystal.



(c) Directions in the cubic crystal system.

Figure 1.40

For example, if

$$x_0, y_0, z_0 \quad \text{are} \quad \frac{1}{2}a, b, \frac{1}{2}c$$

then *P* is at

$$x_1, y_1, z_1 \quad \text{i.e.,} \quad \frac{1}{2}, 1, \frac{1}{2}$$

We then multiply or divide these numbers until we have the smallest integers (which may include 0). If we call these integers *u*, *v*, and *w*, then the direction is written in square brackets without commas as [*uvw*]. If any integer is a negative number, we use a bar on top of that integer. For the particular direction in Figure 1.40b, we therefore have [121].

Some of the important directions in a cubic lattice are shown in Figure 1.40c. For example, the x , y , and z directions in the cube are $[100]$, $[010]$, and $[001]$, as shown. Reversing a direction simply changes the sign of each index. The negative x , y , and z directions are $[\bar{1}00]$, $[0\bar{1}0]$, and $[00\bar{1}]$, respectively.

Certain directions in the crystal are equivalent because the differences between them are based only on our arbitrary decision for labeling x , y , and z directions. For example, $[100]$ and $[010]$ are different simply because of the way in which we labeled the x and y axes. Indeed, directional properties of a material (e.g., elastic modulus, and dielectric susceptibility) along the edge of the cube $[100]$ are invariably the same as along the other edges, for example, $[010]$ and $[001]$. All of these directions along the edges of the cube constitute a **family of directions**, which is any set of directions considered to be equivalent. We label a family of directions, for example, $[100]$, $[010]$, $[001]$, $[\bar{1}00]$, $[0\bar{1}0]$, and $[00\bar{1}]$ in a cubic crystal. Similarly, the family of diagonal directions in the cube, shown in Figure 1.40c, is denoted $\langle 111 \rangle$.

We also frequently need to describe a particular plane in a crystal. Figure 1.41 shows a general unit cell with a plane to be labeled. We use the following convention, called the **Miller indices of a plane**, for this purpose.

We take the intercepts x_0 , y_0 , and z_0 of the plane on the x , y , and z axes, respectively. If the plane passes through the origin, we can use another convenient parallel plane, or simply shift the origin to another point. All planes that have been shifted by a lattice parameter have identical Miller indices.

We express the intercepts x_0 , y_0 , and z_0 in terms of the lattice parameters a , b , and c , respectively, to obtain x_1 , y_1 , and z_1 . We then invert these numbers. Taking the reciprocals, we obtain

$$\frac{1}{x_1}, \frac{1}{y_1}, \frac{1}{z_1}$$

We then clear all fractions, without reducing to lowest integers, to obtain a set of integers, say h , k , and ℓ . We then put these integers into parentheses, without commas, that is, (hkl) . For the plane in Figure 1.41a, we have

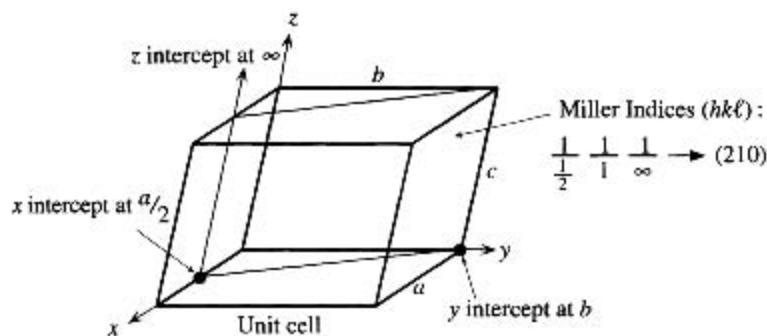
Intercepts x_0 , y_0 , and z_0 are $\frac{1}{2}a$, $1b$, and ∞c .

Intercepts x_1 , y_1 , and z_1 , in terms of a , b , and c , are $\frac{1}{2}$, 1 , and ∞ .

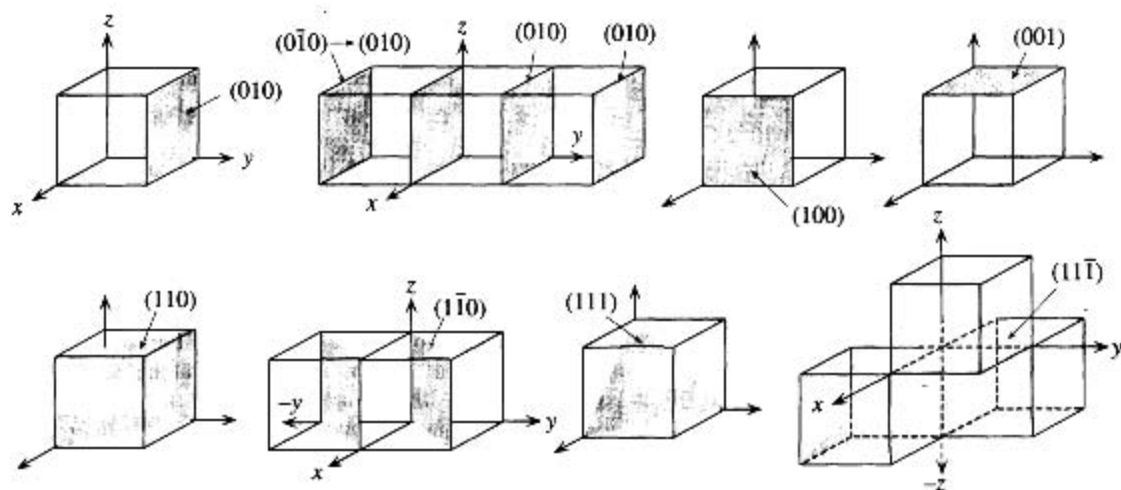
Reciprocals $1/x_1$, $1/y_1$, and $1/z_1$ are $1/\frac{1}{2}$, $1/1$, $1/\infty = 2, 1, 0$.

This set of numbers does not have fractions, so it is not necessary to clear fractions. Hence, the Miller indices (hkl) are (210) .

If there is a negative integer due to a negative intercept, a bar is placed across the top of the integer. Also, if parallel planes differ only by a shift that involves a multiple number of lattice parameters, then these planes may be assigned the same Miller indices. For example, the plane $(0\bar{1}0)$ is the xz plane that cuts the y axis at $-b$. If we shift the plane along y by two lattice parameters ($2b$), it will cut the y axis at b and the Miller indices will become (010) . In terms of the unit cell, the $(0\bar{1}0)$ plane is the same as the (010) plane, as shown in Figure 1.41b. Note that not all parallel planes are



(a) Identification of a plane in a crystal



(b) Various planes in the cubic lattice.

Figure 1.41 Labeling of crystal planes and typical examples in the cubic lattice.

identical. Planes can have the same Miller indices *only* if they are separated by a multiple of the lattice parameter. For example, the (010) plane is not identical to the (020) plane, even though they are geometrically parallel. In terms of the unit cell, plane (010) is a face of the unit cell cutting the y axis at b , whereas (020) is a plane that is halfway inside the unit cell, cutting the y axis at $\frac{1}{2}b$. The planes contain different numbers of atoms. The (020) plane cannot be shifted by the lattice parameter b to coincide with plane (010).

It is apparent from Figure 1.41b that in the case of the cubic crystal, the $[hkl]$ direction is always perpendicular to the (hkl) plane.

Certain planes in the crystal belong to a **family of planes** because their indices differ only as a consequence of the arbitrary choice of axis labels. For example, the indices of the (100) plane become (010) if we switch the x and y axes. All the (100),

(010), and (001) planes, and hence the parallel $(\bar{1}00)$, $(0\bar{1}0)$, $(00\bar{1})$ planes, form a family of planes, conveniently denoted by curly brackets as $\{100\}$.

Frequently we need to know the number of atoms per unit area on a given plane (hkl) . For example, if the surface concentration of atoms is high on one plane, then that plane may encourage oxide growth more rapidly than another plane where there are less atoms per unit area. **Planar concentration of atoms** is the number of atoms per unit area, that is, the surface concentration of atoms, on a given plane in the crystal. Among the $\{100\}$, $\{110\}$, and $\{111\}$ planes in FCC crystals, the most densely packed planes, those with the highest planar concentration, are $\{111\}$ planes and the least densely packed are $\{110\}$.

EXAMPLE 1.14

MILLER INDICES AND PLANAR CONCENTRATION Consider the plane shown in Figure 1.42a, which passes through one side of a face and the center of an opposite face in the FCC lattice. The plane passes through the origin at the lower-left rear corner. We therefore shift the origin to say point O' at the lower-right rear corner of the unit cell. In terms of a , the plane cuts the x , y , and z axes at ∞ , -1 , $\frac{1}{2}$, respectively. We take the reciprocals to obtain, 0 , -1 , 2 . Therefore, the Miller indices are $(0\bar{1}2)$.

To calculate the planar concentration $n_{(hkl)}$ on a given (hkl) plane, we consider a bound area A of the (hkl) plane within the unit cell as in Figure 1.42b. Only atoms whose centers lie on A are involved in $n_{(hkl)}$. For each atom, we then evaluate what portion of the atomic cross section (a circle in two dimensions) cut by the plane (hkl) is contained within A . Consider the Cu FCC crystal with $a = 0.3620$ nm.

The (100) plane corresponds to a cube face and has an area $A = a^2$. There is one full atom at the center; that is, the (100) plane cuts through one full atom, one full circle in two dimensions, at the face center as in Figure 1.42b. However, not all corner atoms are within A . Only a quarter of a circle is within the bound area A in Figure 1.42b.

$$\text{Number of atoms in } A = (4 \text{ corners}) \times \left(\frac{1}{4} \text{ atom}\right) + 1 \text{ atom at face center} = 2$$

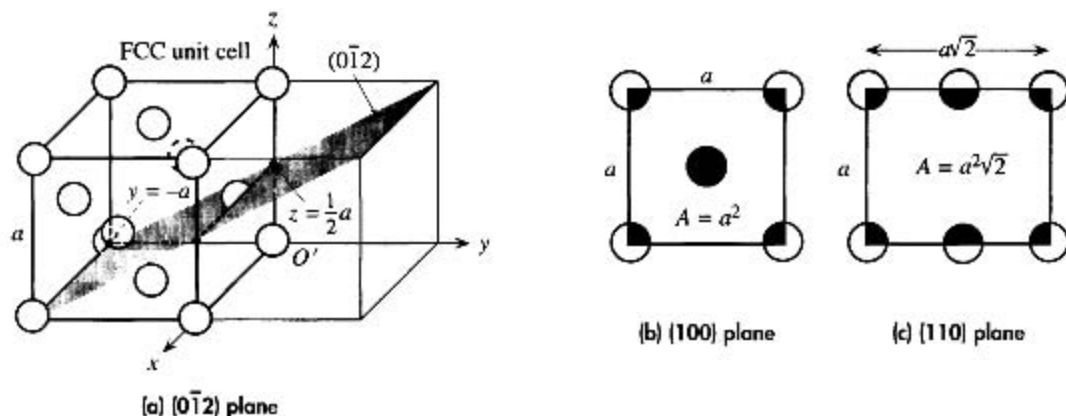


Figure 1.42 The $(0\bar{1}2)$ plane and planar concentrations in an FCC crystal.

Planar concentration $n_{(100)}$ of (100) is

$$n_{(100)} = \frac{4\left(\frac{1}{4}\right) + 1}{a^2} = \frac{2}{a^2} = \frac{2}{(0.3620 \times 10^{-9} \text{ m})^2} = 15.3 \text{ atoms nm}^{-2}$$

Consider the (110) plane as in Figure 1.42c. The number of atoms in the area $A = (a)(a\sqrt{2})$ defined by two face diagonals and two cube sides is

$$(4 \text{ corners}) \times \left(\frac{1}{4} \text{ atom}\right) + (2 \text{ face diagonals}) \times \left(\frac{1}{2} \text{ atom at diagonal center}\right) = 2$$

Planar concentration on (110) is

$$n_{(110)} = \frac{4\left(\frac{1}{4}\right) + 2\left(\frac{1}{2}\right)}{(a)(a\sqrt{2})} = \frac{2}{a^2\sqrt{2}} = 10.8 \text{ atoms nm}^{-2}$$

Similar for the (111) plane, $n_{(111)}$ is $17.0 \text{ atoms nm}^{-2}$. Clearly the (111) planes are the most and (110) planes are the least densely packed among the (100), (110), and (111) planes.

1.8.3 ALLOTROPY AND CARBON

Certain substances can have more than one crystal structure, iron being one of the best-known examples. This characteristic is termed **polymorphism** or **allotropy**. Below 912°C , iron has the BCC structure and is called α -Fe. Between 912°C and 1400°C , iron has the FCC structure and is called γ -Fe. Above 1400°C , iron again has the BCC structure and is called δ -Fe. Since iron has more than one crystal structure, it is called **polymorphic**. Each iron crystal structure is an allotrope or a polymorph.

The allotropes of iron are all metals. Furthermore, one allotrope changes to another at a well-defined temperature called a **transition temperature**, which in this case is 912°C .

Many substances have allotropes that exhibit widely different properties. Moreover, for some polymorphic substances, the transformation from one allotrope to another cannot be achieved by a change of temperature, but requires the application of pressure, as in the transformation of graphite to diamond.

Carbon has three important crystalline allotropes: diamond, graphite, and the newly discovered **buckminsterfullerene**. These crystal structures are shown in Figure 1.43a, b and c, respectively, and their properties are summarized in Table 1.4. Graphite is the carbon form that is stable at room temperature. Diamond is the stable form at very high pressures. Once formed, diamond continues to exist at atmospheric pressures and below about 900°C , because the transformation rate of diamond to graphite is virtually zero under these conditions. Graphite and diamond have widely differing properties, which lead to diverse applications. For example, graphite is an electrical conductor, whereas diamond is an insulator. Diamond is the hardest substance known. On the other hand, the carbon layers in graphite can readily slide over each other under shear stresses, because the layers are only held together by weak secondary bonds (van der Waals bonds). This is the reason for graphite's lubricating properties.

Buckminsterfullerene is another polymorph of carbon. In the buckminsterfullerene molecule (called the "buckyball"), 60 carbon atoms bond with each other to form a

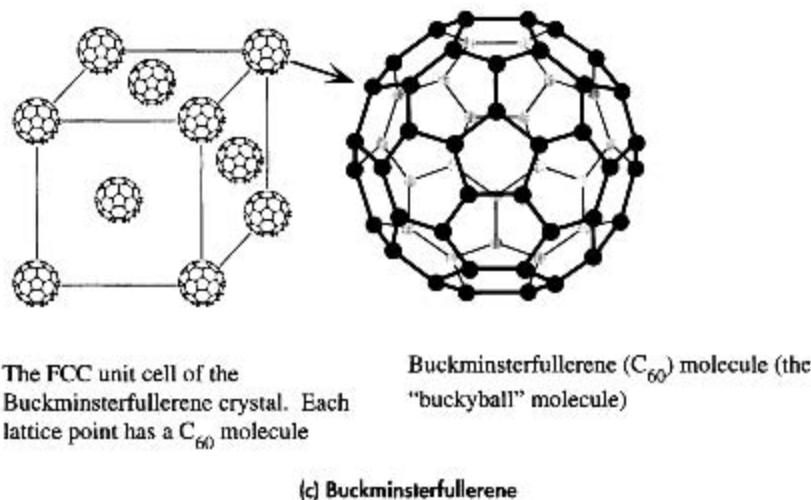
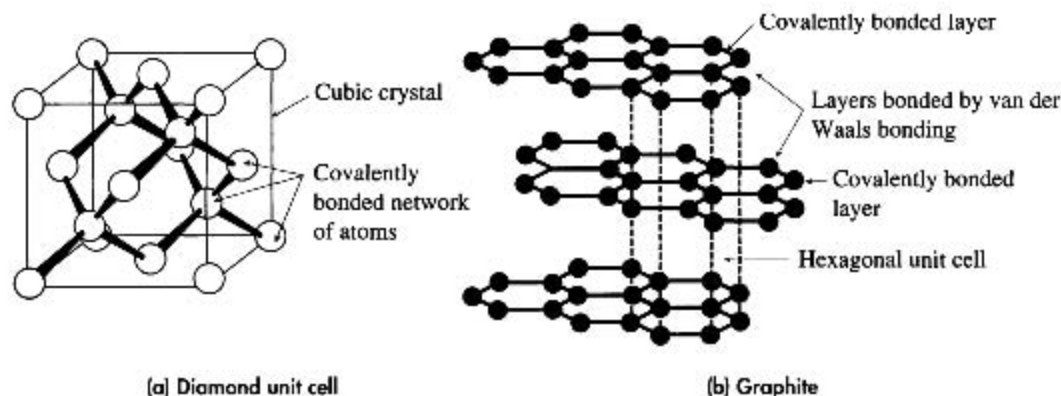


Figure 1.43 The three allotropes of carbon.

perfect soccer ball-type molecule. The C_{60} molecule has 12 pentagons and 20 hexagons joined together to form a spherical molecule, with each C atom at a corner, as depicted in Figure 1.43c. The molecules are produced in the laboratory by a carbon arc in a partial atmosphere of an inert gas (He); they are also found in the soot of partial combustion. The crystal form of buckminsterfullerene has the FCC structure, with each C_{60} molecule occupying a lattice point and being held together by van der Waals forces, as shown in Figure 1.43c. The Buckminsterfullerene crystal is a semiconductor, and its compounds with alkali metals, such as K_3C_{60} , exhibit superconductivity at low temperatures (below 18 K). Mechanically, it is a soft material.

Diamond, graphite, and the fullerene crystals are not the only crystalline allotropes of carbon, and neither are they the only structural forms of carbon. For example, **lonsdaleite**, which is another crystalline allotrope, is *hexagonal diamond*

Table 1.4 Crystalline allotropes of carbon [ρ is the density and Y is the elastic modulus or Young's modulus]

	Graphite	Diamond	Buckminsterfullerene Crystal
Structure	Covalent bonding within layers. Van der Waals bonding between layers. Hexagonal unit cell.	Covalently bonded network. Diamond crystal structure.	Covalently bonded C_{60} spheroidal molecules held in an FCC crystal structure by van der Waals bonding.
Electrical and thermal properties	Good electrical conductor. Thermal conductivity comparable to metals.	Very good electrical insulator. Excellent thermal conductor, about five times more than silver or copper.	Semiconductor. Compounds with alkali metals (e.g., K_3C_{60}) exhibit superconductivity.
Mechanical properties	Lubricating agent. Machinable. Bulk graphite: $Y \approx 27 \text{ GPa}$ $\rho = 2.25 \text{ g cm}^{-3}$	The hardest material. $Y = 827 \text{ GPa}$ $\rho = 3.25 \text{ g cm}^{-3}$	Mechanically soft. $Y \approx 18 \text{ GPa}$ $\rho = 1.65 \text{ g cm}^{-3}$
Comment	Stable allotrope at atmospheric pressure	High-pressure allotrope.	Laboratory synthesized. Occurs in the soot of partial combustion.
Uses, potential uses	Metallurgical crucibles, welding electrodes, heating elements, electrical contacts, refractory applications.	Cutting tool applications. Diamond anvils. Diamond film coated drills, blades, bearings, etc. Jewelry. Heat conductor for ICs. Possible thin-film semiconductor devices, as the charge carrier mobilities are large.	Possible future semiconductor or superconductivity applications.

in which each C atom covalently bonds to four neighbors, as in diamond, but the crystal structure has hexagonal symmetry. (It forms from graphite on meteors when the meteors impact the Earth; currently it is only found in Arizona.) **Amorphous carbon** has no crystal structure (no long-range order), so it is not a crystalline allotrope, but many scientists define it as a form or phase of carbon, or as a structural "allotrope." The recently discovered **carbon nanotubes** are thin and long carbon tubes, perhaps 10 to 100 microns long but only several nanometers in diameter, hence the name *nanotube*. They are tubes made from rolling a graphite sheet into a tube and then capping the ends with hemispherical buckyballs. The carbon tube is really a single macromolecule rather than a crystal in its traditional sense¹²; it is a structural form of carbon. Carbon nanotubes have many interesting and remarkable properties and offer much potential for various applications in electronics; the most topical currently being carbon nanotube field emission devices. (Chapter 4 has an example.)

¹² It is possible to define a unit cell on the surface of a carbon nanotube and apply various crystalline concepts, as some scientists have done. To date, however, there seems to be no single crystal of carbon nanotubes in the same way that there is a fullerene crystal in which the C_{60} molecules are bonded to form an FCC structure.

1.9 CRYSTALLINE DEFECTS AND THEIR SIGNIFICANCE

By bringing all the atoms together to try to form a perfect crystal, we lower the total potential energy of the atoms as much as possible for that particular structure. What happens when the crystal is grown from a liquid or vapor; do you always get a perfect crystal? What happens when the temperature is raised? What happens when impurities are added to the solid?

There is no such thing as a perfect crystal. We must therefore understand the types of defects that can exist in a given crystal structure. Quite often, key mechanical and electrical properties are controlled by these defects.

1.9.1 POINT DEFECTS: VACANCIES AND IMPURITIES

Above the absolute zero temperature, all crystals have atomic vacancies or atoms missing from lattice sites in the crystal structure. The vacancies exist as a requirement of thermal equilibrium and are called **thermodynamic defects**. Vacancies introduce disorder into the crystal by upsetting the perfect periodicity of atomic arrangements.

We know from the kinetic molecular theory that all the atoms in a crystal vibrate about their equilibrium positions with a distribution of energies, a distribution that closely resembles the Boltzmann distribution. At some instant, there may be one atom with sufficient energy to break its bonds and jump to an adjoining site on the surface, as depicted in Figure 1.44. This leaves a vacancy behind, just below the surface. This vacancy can then diffuse into the bulk of the crystal, because a neighboring atom can diffuse into it.

This latter process of vacancy creation has been shown to be a sequence of events in Figure 1.44. Suppose that E_v is the average energy required to create such a vacancy. Then only a fraction, $\exp(-E_v/kT)$, of all the atoms in the crystal can have

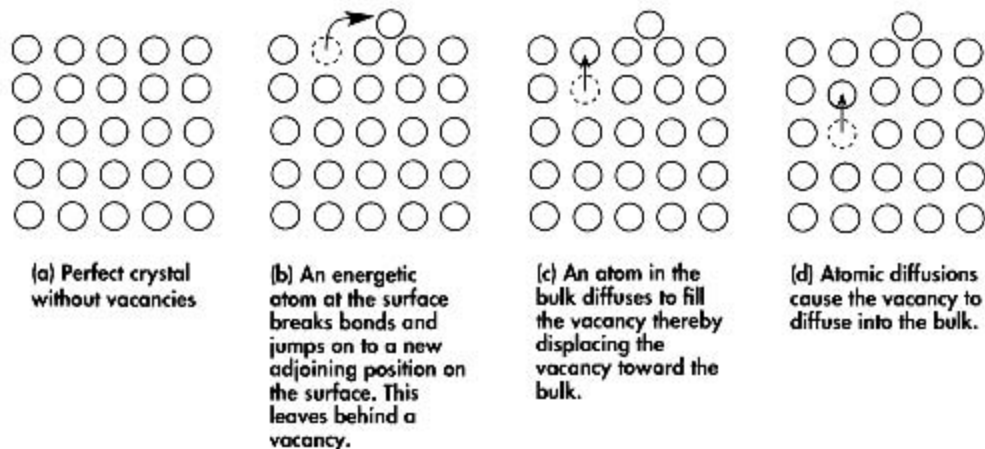
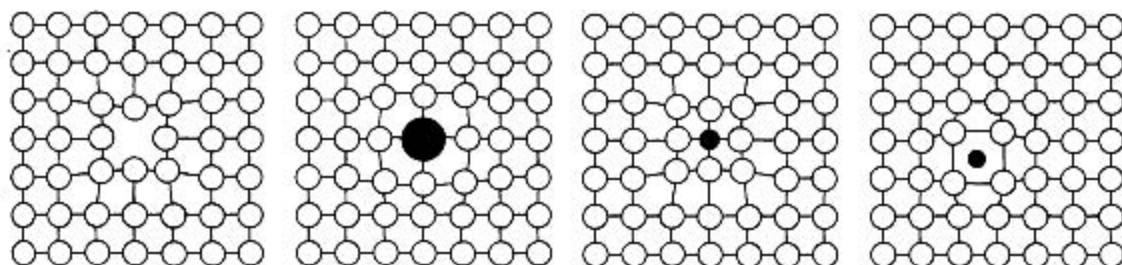


Figure 1.44 Generation of a vacancy by the diffusion of an atom to the surface and the subsequent diffusion of the vacancy into the bulk.



(a) A vacancy in the crystal.

(b) A substitutional impurity in the crystal. The impurity atom is larger than the host atom.

(c) A substitutional impurity in the crystal. The impurity atom is smaller than the host atom.

(d) An interstitial impurity in the crystal. The impurity occupies an empty space between host atoms.

Figure 1.45 Point defects in the crystal structure.

The regions around the point defect become distorted; the lattice becomes strained.

sufficient energy to create vacancies. If the number of atoms per unit volume in the crystal is N , then the vacancy concentration n_v is given by¹³

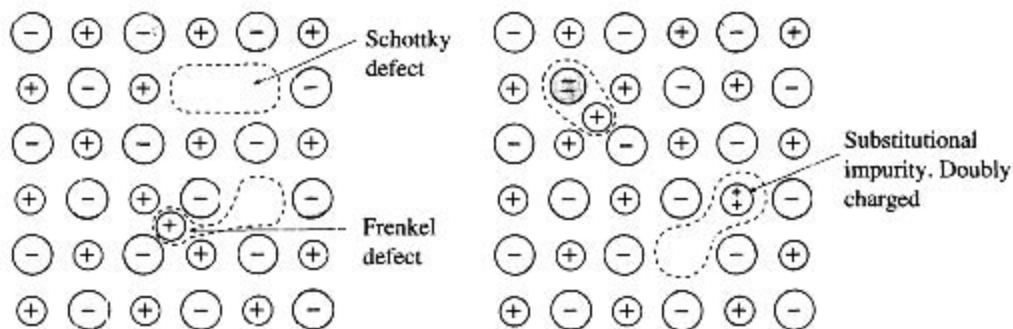
$$n_v = N \exp\left(-\frac{E_v}{kT}\right) \quad [1.35]$$

*Equilibrium
concentration
of vacancies*

At all temperatures above absolute zero, there will always be an equilibrium concentration of vacancies, as dictated by Equation 1.35. Although we considered only one possible vacancy creation process in Figure 1.44 there are other processes that also create vacancies. Furthermore, we have shown the vacancy to be the same size in the lattice as the missing atom, which is not entirely true. The neighboring atoms around a vacancy close in to take up some of the slack, as shown in Figure 1.45a. This means that the crystal lattice around the vacancy is distorted from the perfect arrangement over a few atomic dimensions. The vacancy volume is therefore smaller than the volume of the missing atom.

Vacancies are only one type of **point defect** in a crystal structure. Point defects generally involve lattice changes or distortions of a few atomic distances, as depicted in Figure 1.45. The crystal structure may contain impurities, either naturally or as a consequence of intentional addition, as in the case of silicon crystals grown for microelectronics. If the impurity atom substitutes directly for the host atom, the result is called a **substitutional impurity** and the resulting crystal structure is that of a **substitutional solid solution**, as shown in Figure 1.45b and c. When a Si crystal is “doped” with small amounts of arsenic (As) atoms, the As atoms substitute directly for the Si atoms in the Si crystal; that is, the arsenic atoms are substitutional impurities. The impurity atom can also place itself in an interstitial site, that is, in a void between the host atoms, as

¹³ The proper derivation of the vacancy concentration involves considering thermodynamics and equilibrium concepts. In the actual thermodynamic expression, the pre-exponential term in Equation 1.35 is not unity but a factor that depends on the change in the entropy of the crystal upon vacancy creation. For nearly all practical purposes Equation 1.35 is sufficient.



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

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

Figure 1.46 Point defects in ionic crystals.

carbon does in the BCC iron crystal. In that case, the impurity is called an **interstitial impurity**, as shown in Figure 1.45d.

In general, the impurity atom will have both a different valency and a different size. It will therefore distort the lattice around it. For example, if a substitutional impurity atom is larger than the host atom, the neighboring host atoms will be pushed away, as in Figure 1.45b. The crystal region around an impurity is therefore distorted from the perfect periodicity and the lattice is said to be **strained around a point defect**. A smaller substitutional impurity atom will pull in the neighboring atoms, as in Figure 1.45c. Typically, interstitial impurities tend to be small atoms compared to the host atoms, a typical example being the small carbon atom in the BCC iron crystal.

In an ionic crystal, such as NaCl, which consists of anions (Cl^-) and cations (Na^+), one common type of defect is called a **Schottky defect**. This involves a missing cation-anion pair (which may have migrated to the surface), so the neutrality is maintained, as indicated in Figure 1.46a. These Schottky defects are responsible for the major optical and electrical properties of alkali halide crystals. Another type of defect in the ionic crystal is the **Frenkel defect**, which occurs when a host ion is displaced into an interstitial position, leaving a vacancy at its original site. The interstitial ion and the vacancy pair constitute the Frenkel defect, as identified in Figure 1.46a. For the AgCl crystal, which has predominantly Frenkel defects, an Ag^+ is in an interstitial position. The concentration of such Frenkel defects is given by Equation 1.35, with an appropriate defect creation energy E_{defect} instead of E_v .

Ionic crystals can also have substitutional and interstitial impurities that become ionized in the lattice. Overall, the ionic crystal must be neutral. Suppose that an Mg^{2+} ion substitutes for an Na^+ ion in the NaCl crystal, as depicted in Figure 1.46b. Since the overall crystal must be neutral, either one Na^+ ion is missing somewhere in the crystal, or an additional Cl^- ion exists in the crystal. Similarly, when a doubly charged negative ion, such as O^{2-} , substitutes for Cl^- , there must either be an additional cation (usually in an interstitial site) or a missing Cl^- somewhere in order to maintain charge

neutrality in the crystal. The most likely type of defect depends on the composition of the ionic solid and the relative sizes and charges of the ions.

VACANCY CONCENTRATION IN A METAL The energy of formation of a vacancy in the aluminum crystal is about 0.70 eV. Calculate the fractional concentration of vacancies in Al at room temperature, 300 K, and very close to its melting temperature 660 °C. What is the vacancy concentration at 660 °C given that the atomic concentration in Al is about $6.0 \times 10^{22} \text{ cm}^{-3}$?

EXAMPLE 1.15**SOLUTION**

Using Equation 1.35, the fractional concentration of vacancies are as follows:

At 300 °C,

$$\frac{n_v}{N} = \exp\left(-\frac{E_v}{kT}\right) = \exp\left[-\frac{(0.70 \text{ eV})(1.6 \times 10^{-19} \text{ J eV}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K})}\right] \\ = 1.7 \times 10^{-12}$$

At 660 °C or 933 K,

$$\frac{n_v}{N} = \exp\left(-\frac{E_v}{kT}\right) = \exp\left[-\frac{(0.70 \text{ eV})(1.6 \times 10^{-19} \text{ J eV}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(933 \text{ K})}\right] \\ = 1.7 \times 10^{-4}$$

That is, almost 1 in 6000 atomic sites is a vacancy. The atomic concentration N in Al is about $6.0 \times 10^{22} \text{ cm}^{-3}$, which means that the vacancy concentration n_v at 660 °C is

$$n_v = (6.0 \times 10^{22} \text{ cm}^{-3})(1.7 \times 10^{-4}) = 1.0 \times 10^{19} \text{ cm}^{-3}$$

The mean vacancy separation (on the order of $n_v^{-1/3}$) at 660 °C is therefore roughly 5 nm. The mean atomic separation in Al is $\sim 0.3 \text{ nm}$ ($\sim N^{-1/3}$), so the mean separation between vacancies is only about 20 atomic separations! (A more accurate version of Equation 1.35, with an entropy term, shows that the vacancy concentration is even higher than the estimate in this example.) The increase in the linear thermal expansion coefficient of a metal with temperature near its melting temperature, as shown for Mo in Figure 1.20, has been attributed to the generation of vacancies in the crystal.

VACANCY CONCENTRATION IN A SEMICONDUCTOR The energy of vacancy formation in the Ge crystal is about 2.2 eV. Calculate the fractional concentration of vacancies in Ge at 938 °C, just below its melting temperature. What is the vacancy concentration given that the atomic mass M_{at} and density ρ of Ge are 72.64 g mol^{-1} and 5.32 g cm^{-3} , respectively? Neglect the change in the density with temperature which is small compared with other approximations in Equation 1.35.

EXAMPLE 1.16**SOLUTION**

Using Equation 1.34, the fractional concentration of vacancies at 938 °C or 1211 K is

$$\frac{n_v}{N} = \exp\left(-\frac{E_v}{kT}\right) = \exp\left[-\frac{(2.2 \text{ eV})(1.6 \times 10^{-19} \text{ J eV}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(1211 \text{ K})}\right] = 7.0 \times 10^{-10}$$

which is orders of magnitude less than that for Al at its melting temperature in Example 1.15; vacancies in covalent crystals cost much more energy than those in metals.

The number of Ge atoms per unit volume is

$$N = \frac{\rho N_A}{M_u} = \frac{(5.32 \text{ g cm}^{-3})(6.022 \times 10^{23} \text{ g mol}^{-1})}{72.64 \text{ g mol}^{-1}} = 4.41 \times 10^{22} \text{ cm}^{-3}$$

so that at 938 °C,

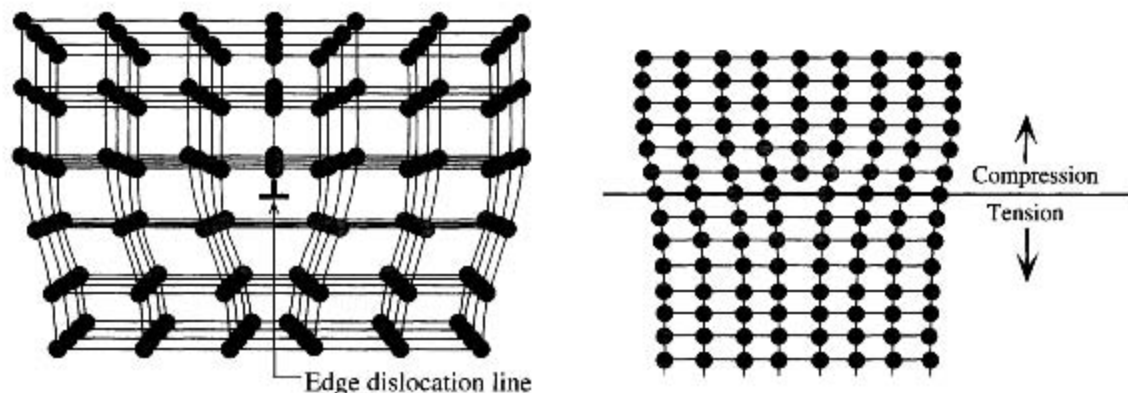
$$n_v = (4.4 \times 10^{22} \text{ cm}^{-3})(7.0 \times 10^{-10}) = 3.1 \times 10^{13} \text{ cm}^{-3}$$

Only 1 in 10^9 atoms is a vacancy.

1.9.2 LINE DEFECTS: EDGE AND SCREW DISLOCATIONS

A line defect is formed in a crystal when an atomic plane terminates within the crystal instead of passing all the way to the end of the crystal, as depicted in Figure 1.47a. The edge of this short plane of atoms is therefore like a line running inside the crystal. The planes neighboring (*i.e.*, above) this short plane are dislocated (displaced) with respect to those below the line. We therefore call this type of defect an **edge dislocation** and use an inverted T symbol. The vertical line corresponds to the half-plane of atoms in the crystal, as illustrated in Figure 1.47a. It is clear that the atoms around the dislocation line have been effectively displaced from their perfect-crystal equilibrium positions, which results in atoms being out of registry above and below the dislocation. The atoms above the dislocation line are pushed together, whereas those below it are pulled apart, so there are regions of compression and tension above and below the dislocation line, respectively, as depicted by the shaded region around the dislocation line in Figure 1.47b. Therefore, around a dislocation line, we have a **strain field** due to the stretching or compressing of bonds.

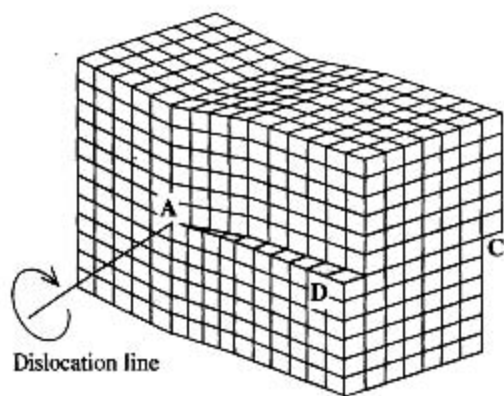
The energy required to create a dislocation is typically in the order of 100 eV per nm of dislocation line. On the other hand, it takes only a few eV to form a point defect,



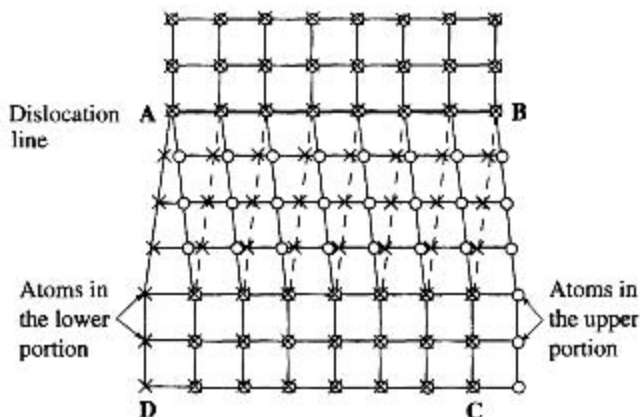
(a) Dislocation is a line defect. The dislocation shown runs into the paper.

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

Figure 1.47 Dislocation in a crystal. This is a line defect, which is accompanied by lattice distortion and hence a lattice strain around it.



(a) A screw dislocation in a crystal



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

Figure 1.48 A screw dislocation, which involves shearing one portion of a perfect crystal with respect to another, on one side of a line [AB].

which is a few nanometers in dimension. In other words, forming a number of point defects is energetically more favorable than forming a dislocation. Dislocations are not *equilibrium* defects. They normally arise when the crystal is deformed by stress, or when the crystal is actually being grown.

Another type of dislocation is the **screw dislocation**, which is essentially a shearing of one portion of the crystal with respect to another, by one atomic distance, as illustrated in Figure 1.48a. The displacement occurs on either side of the **screw dislocation line**. The circular arrow around the line symbolizes the screw dislocation. As we move away from the dislocation line, the atoms in the upper portion become more out of registry with those below; at the edge of the crystal, this displacement is one atomic distance, as illustrated in Figure 1.48b.

Both edge and screw dislocations are generally created by stresses resulting from thermal and mechanical processing. A line defect is not necessarily either a pure edge or a pure screw dislocation; it can be a mixture, as depicted in Figure 1.49. Screw dislocations frequently occur during crystal growth, which involves atomic stacking on the surface of a crystal. Such dislocations aid crystallization by providing an additional "edge" to which the incoming atoms can attach, as illustrated in Figure 1.50. To explain, if an atom arrives at the surface of a perfect crystal, it can only attach to one atom in the plane below. However, if there is a screw dislocation, the incoming atom can attach to an edge and thereby form more bonds; hence, it can lower its potential energy more than anywhere else on the surface. With incoming atoms attaching to the edges, the growth occurs spirally around the screw dislocation, and the final crystal surface reflects this spiral growth geometry.

The phenomenon of **plastic** or **permanent deformation** of a metal depends totally on the presence and motions of dislocations, as discussed in elementary books on the mechanical properties of materials. In the case of electrical properties of metals,

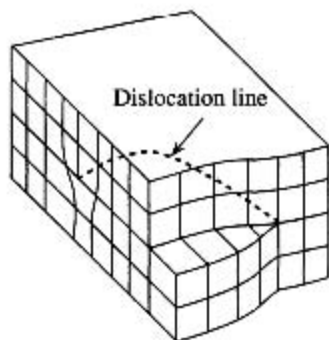


Figure 1.49 A mixed dislocation.

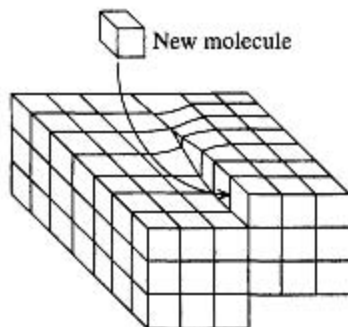


Figure 1.50 Screw dislocation aids crystal growth because the newly arriving atom can attach to two or three atoms instead of one atom and thereby form more bonds.



Growth spiral on the surface of a polypropylene crystal due to screw dislocation aided crystal growth.

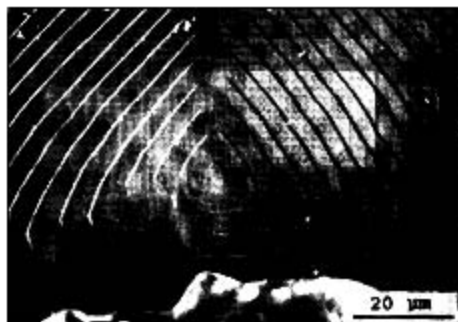
SOURCE: Photo by Phillip Geil, Courtesy of Case Western Reserve University.

we will see in Chapter 2 that dislocations increase the resistivity of materials, cause significant leakage current in a *pn* junction, and give rise to unwanted noise in various semiconductor devices. Fortunately, the occurrence of dislocations in semiconductor crystals can be controlled and nearly eliminated. In a metal interconnection line on a chip, there may be an average of 10^4 – 10^5 dislocation lines per mm^2 of crystal, whereas a silicon crystal wafer that is carefully grown may typically have only 1 dislocation line per mm^2 of crystal.

1.9.3 PLANAR DEFECTS: GRAIN BOUNDARIES

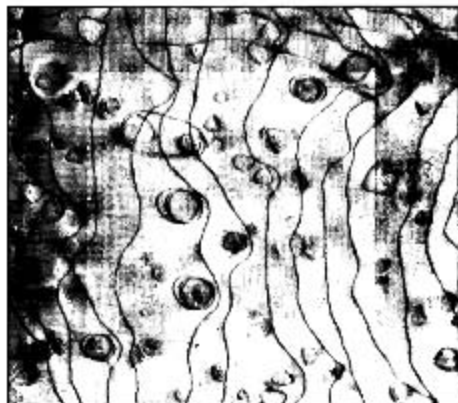
Many materials are polycrystalline; that is, they are composed of many small crystals oriented in different directions. In fact, the growth of a flawless single crystal from what is called the **melt** (liquid) requires special skills, in addition to scientific knowledge. When a liquid is cooled to below its freezing temperature, solidification does not occur at every point; rather, it occurs at certain sites called **nuclei**, which are small crystal-like structures containing perhaps 50 to 100 atoms. Figure 1.51a to c depicts a typical solidification process from the melt. The liquid atoms adjacent to a nucleus diffuse into the nucleus, thereby causing it to grow in size to become a small crystal, or a crystallite, called a **grain**. Since the nuclei are randomly oriented when they are formed, the grains have random crystallographic orientations during crystallite growth. As the liquid between the grains is consumed, some grains meet and obstruct each other. At the end of solidification, therefore, the whole structure has grains with irregular shapes and orientations, as shown in Figure 1.51c.

It is apparent from Figure 1.51c that in contrast to a single crystal, a polycrystalline material has grain boundaries where differently oriented crystals meet. As indicated in Figure 1.52, the atoms at the grain boundaries obviously cannot follow their



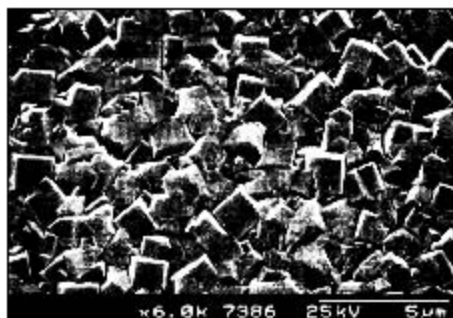
The photograph of the surface of a synthetic diamond grown on the (111) surface of natural diamond from sodium carbonate solvent at 5.5 GPa and 1600 °C.

SOURCE: Courtesy of Dr. Hisao Kanda, National Institute for Materials Science, Ibaraki, Japan.



Dislocations can be seen by examining a thin slice of the sample under a transmission electron microscope (TEM). They appear as dark lines and loops as shown here in a Ni-Si alloy single crystal. The loop dislocations are around Ni₃Si particles inside the crystal. The sample had been mechanically deformed, which generates dislocations.

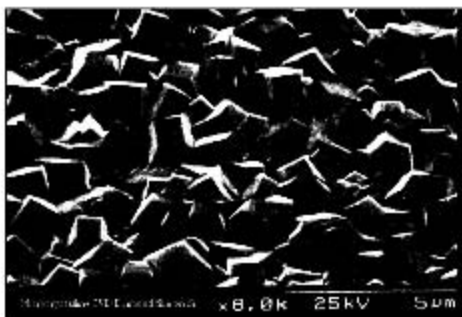
SOURCE: Courtesy of Professor John Humphreys, UMIST, England. (J. Humphreys and V. Ramaswamy in *High Voltage Electron Microscopy*, ed. P. R. Swann, C. J. Humphreys and M. J. Goringe, New York: Academic Press, 1974, p. 26.)



Left: A polycrystalline diamond film on the (100) surface of a single crystal silicon wafer. The film thickness is 6 microns and the SEM magnification is 6000.

Right: A 6-micron-thick CVD diamond film grown on a single crystal silicon wafer. SEM magnification is 8000.

SOURCE: Courtesy of Dr. Paul May, The School of Chemistry, University of Bristol, England.



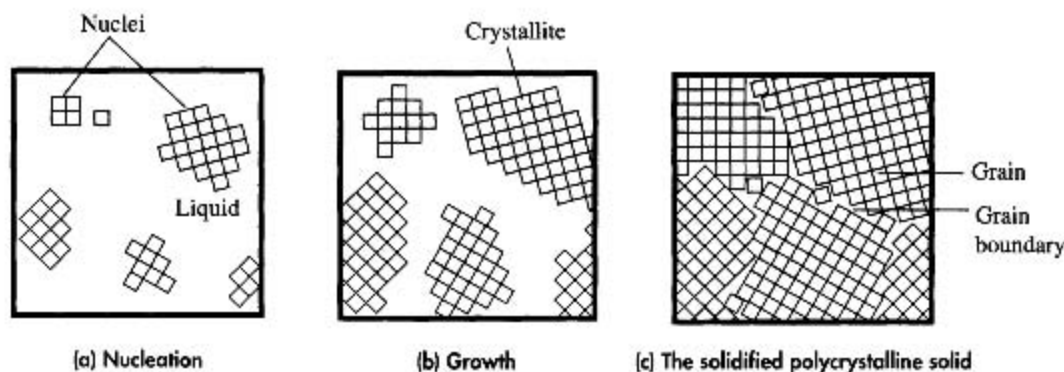


Figure 1.51 Solidification of a polycrystalline solid from the melt. For simplicity, cubes represent atoms.

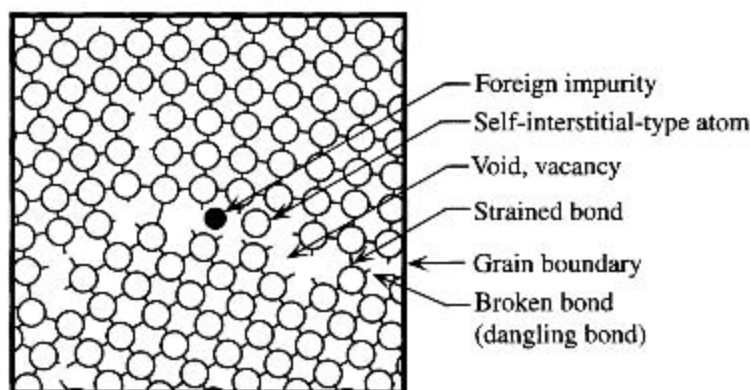


Figure 1.52 The grain boundaries have broken bonds, voids, vacancies, strained bonds, and interstitial-type atoms.

The structure of the grain boundary is disordered, and the atoms in the grain boundaries have higher energies than those within the grains.

natural bonding habits, because the crystal orientation suddenly changes across the boundary. Therefore, there are both voids at the grain boundary and stretched and broken bonds. In addition, in this region, there are misplaced atoms that do not follow the crystalline pattern on either side of the boundary. Consequently, the grain boundary represents a high-energy region per atom with respect to the energy per atom within the bulk of the grains themselves. The atoms can diffuse more easily along a grain boundary because (a) less bonds need to be broken due to the presence of voids and (b) the bonds are strained and easily broken anyway. In many polycrystalline materials, impurities therefore tend to congregate in the grain boundary region. We generally refer to the atomic arrangement in the grain boundary region as being **disordered** due to the presence of the voids and misplaced atoms.

Since the energy of an atom at the grain boundary is greater than that of an atom within the grain, these grain boundaries are nonequilibrium defects; consequently, they try to reduce in size to give the whole structure a lower potential energy. At or around room temperature, the atomic diffusion process is slow; thus, the reduction in the grain boundary is insignificant. At elevated temperatures, however, atomic diffusion allows big grains to grow, at the expense of small grains, which leads to **grain coarsening (grain growth)** and hence to a reduction in the grain boundary area.

Mechanical engineers have learned to control the grain size, and hence the mechanical properties of metals to suit their needs, through various thermal treatment cycles. For electrical engineers, the grain boundaries become important when designing electronic devices based on polysilicon or any polycrystalline semiconductor. For example, in highly polycrystalline materials, particularly thin-film semiconductors (e.g., polysilicon), the resistivity is invariably determined by polycrystallinity, or grain size, of the material, as discussed in Chapter 2.

1.9.4 CRYSTAL SURFACES AND SURFACE PROPERTIES

In describing crystal structures, we assume that the periodicity extends to infinity which means that the regular array of atoms is not interrupted anywhere by the presence of real surfaces of the material. In practice, we know that all substances have real surfaces. When the crystal lattice is abruptly terminated by a surface, the atoms at the surface cannot fulfill their bonding requirements as illustrated in Figure 1.53. For simplicity, the figure shows a Si crystal schematically sketched in two dimensions where each atom in the bulk of the crystal has four covalent bonds, each covalent bond

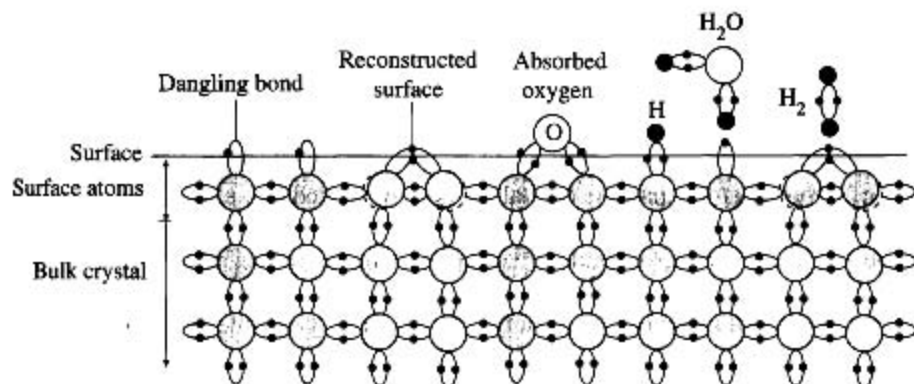


Figure 1.53 At the surface of a hypothetical two-dimensional crystal, the atoms cannot fulfill their bonding requirements and therefore have broken, or dangling, bonds.

Some of the surface atoms bond with each other; the surface becomes reconstructed. The surface can have physisorbed and chemisorbed atoms.

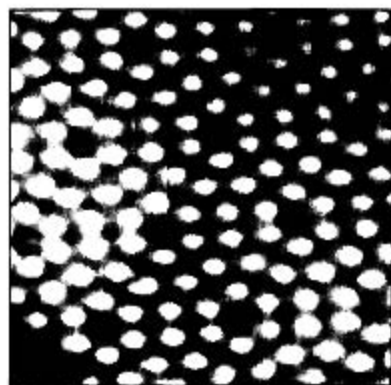
having two electrons.¹⁴ The atoms at the surface are left with **dangling bonds**, bonds that are half full, only having one electron. These dangling bonds are looking for atoms to which they can bond. Two neighboring surface atoms can share each other's dangling bond electrons, that is, form a surface bond with each other. This bonding between surface atoms causes a slight displacement of the surface atoms and leads to a surface that has been **reconstructed**.

Atoms from the environment can also bond with the atoms on the crystal surface. For example, a hydrogen atom can be captured by a dangling bond at the surface to form a chemical bond as a result of which hydrogen becomes **absorbed**. Primary bonding of foreign atoms to a crystal surface is called **chemisorption**. The H atom in Figure 1.53 forms a covalent bond with a Si atom and hence becomes **chemisorbed**. However, the H₂O molecule cannot form a covalent bond, but, because of hydrogen bonding, it can form a secondary bond with a surface Si atom and become **adsorbed**. Secondary bonding of foreign atoms or molecules to a crystal surface is called **physisorption** (*physical adsorption*). Water molecules in the air can readily become adsorbed at the surface of a crystal. Although the figure also shows a physisorbed H₂ molecule as an example, this normally occurs at very low temperatures where crystal vibrations are too weak to quickly dislodge the H₂ molecule. It should be remarked that in many cases, atoms or molecules from the environment become adsorbed at the surface for only a certain period of time; they have a certain sticking or dwell time. For example, at room temperature, inert gases stick to a metal surface only for a duration of the order of microseconds, which is extremely long compared with the vibrational period of the crystal atoms ($\sim 10^{-12}$ seconds). A dangling bond can capture a free electron from the environment if one is available in its vicinity. The same idea applies to a dangling bond at a grain boundary as in Figure 1.52.

At sufficiently high temperatures, some of the absorbed foreign surface atoms can diffuse into the crystal volume to become bulk impurities. Many substances have a natural oxide layer on the surface that starts with the chemical bonding of oxygen atoms to the surface atoms and the subsequent growth of the oxide layer. For example, aluminum surfaces always have a thin aluminum oxide layer. In addition, the surface of the oxide often has adsorbed organic species of atoms usually from machining and handling. The surface condition of a Si crystal wafer in microelectronics is normally controlled by first etching the surface and then oxidizing it at a high temperature to form a SiO₂ **passivating layer** on the crystal surface. This oxide layer is an excellent barrier against the diffusion of impurity atoms into the crystal. (It is also an excellent electrical insulator.)

Figure 1.53 shows only some of the possibilities at the surface of a crystal. Generally the surface structure depends greatly on the mode of surface formation, which invariably involves thermal and mechanical processing, and previous environmental history. One visualization of a crystal surface is based on the **terrace-ledge-kink model**, the so-called **Kossel model**, as illustrated in Figure 1.54. The surface has ledges, kinks, and various imperfections such as holes and dislocations, as well as impurities which can diffuse to and from the surface. The dimensions of the various imperfections (*e.g.*, the step size) depend on the process that generated the surface.

¹⁴ Not all possibilities shown in Figure 1.53 occur in practice; their occurrences depend on the preparation method of the crystal.



Atomic arrangements on a reconstructed (111) surface of a Si crystal as seen by a surface tunneling microscope.

SOURCE: Courtesy of Burleigh Instruments, Inc.

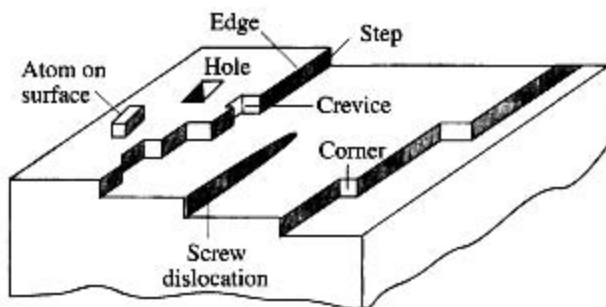
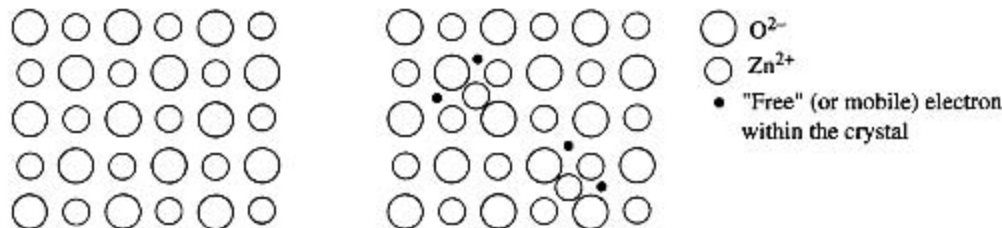


Figure 1.54 Typically, a crystal surface has many types of imperfections, such as steps, ledges, kinks, crevices, holes, and dislocations.

1.9.5 STOICHIOMETRY, NONSTOICHIOMETRY, AND DEFECT STRUCTURES

Stoichiometric compounds are those that have an integer ratio of atoms, for example, as in CaF_2 where two F atoms bond with one Ca atom. Similarly, in the compound ZnO , if there is one O atom for every Zn atom, the compound is stoichiometric, as schematically illustrated in Figure 1.55a. Since there are equal numbers of O^{2-} anions and Zn^{2+} cations, the crystal overall is neutral. It is also possible to have a nonstoichiometric ZnO in which there is excess zinc. This may result if, for example, there is insufficient oxygen during the preparation of the compound. The Zn^{2+} ion has a radius of 0.074 nm, which is about 1.9 times smaller than the O^{2-} anion (radius of 0.14 nm), so it is much easier for a Zn^{2+} ion to enter an interstitial site than the O^{2-} ion or the Zn atom itself, which has a radius of 0.133 nm. Excess Zn atoms therefore occupy interstitial sites as Zn^{2+} cations. Even though the excess zinc atoms are still ionized within the crystal, their lost electrons cannot be taken by oxygen atoms, which are all



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

(b) Nonstoichiometric ZnO crystal with excess Zn in interstitial sites as Zn^{2+} cations

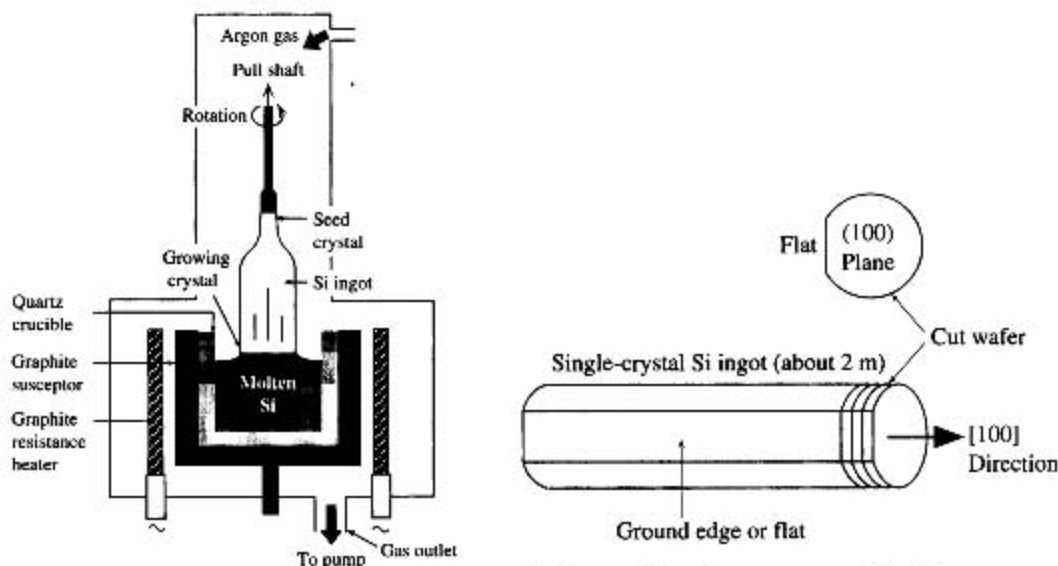
Figure 1.55 Stoichiometry and nonstoichiometry and the resulting defect structure.

O^{2-} anions, as indicated in Figure 1.55b. Thus, the nonstoichiometric ZnO with excess Zn has Zn^{2+} cations in interstitial sites and mobile electrons within the crystal, which can contribute to the conduction of electricity. Overall, the crystal is neutral, as the number of Zn^{2+} ions is equal to the number of O^{2-} ions plus two electrons from each excess Zn. The structure shown in Figure 1.55b is a defect structure, since it deviates from the stoichiometry.

1.10 SINGLE-CRYSTAL CZOCHRALSKI GROWTH

The fabrication of discrete and integrated circuit (IC) solid-state devices requires semiconductor crystals with impurity concentrations as low as possible and crystals that contain very few imperfections. A number of laboratory techniques are available for growing high-purity semiconductor crystals. Generally, they involve either solidification from the melt or condensation of atoms from the vapor phase. The initial process in IC fabrication requires large single-crystal wafers that are typically 15 cm in diameter and 0.6 mm thick. These wafers are cut from a long, cylindrical single Si crystal (typically, 1–2 m in length).

Large, single Si crystals for IC fabrication are often grown by the **Czochralski method**, which involves growing a single-crystal ingot from the melt, using solidification on a seed crystal, as schematically illustrated in Figure 1.56a. Molten Si is held in a quartz (crystalline SiO_2) crucible in a graphite susceptor, which is either heated by



(a) Schematic illustration of the growth of a single-crystal Si ingot by the Czochralski technique.

(b) The crystallographic orientation of the silicon ingot is marked by grinding a flat. The ingot can be as long as 2 m. Wafers are cut using a rotating annular diamond saw. Typical wafer thickness is 0.6–0.7 mm.

Figure 1.56



Silicon ingot being pulled from the melt in a Czochralski crystal drawer.

SOURCE: Courtesy of MEMC Electronic Materials, Inc.

a graphite resistance heater or by a radio frequency induction coil (a process called **RF heating**).¹⁵ A small dislocation-free crystal, called a **seed**, is lowered to touch the melt and then slowly pulled out of the melt; a crystal grows by solidifying on the seed crystal. The seed is rotated during the pulling stage, to obtain a cylindrical ingot. To suppress evaporation from the melt and prevent oxidation, argon gas is passed through the system.

Initially, as the crystal is withdrawn, its cross-sectional area increases; it then reaches a constant value determined by the temperature gradients, heat losses, and the rate of pull. As the melt solidifies on the crystal, heat of fusion is released and must be conducted away; otherwise, it will raise the temperature of the crystal and remelt it. The area of the melt–crystal interface determines the rate at which this heat can be conducted away through the crystal, whereas the rate of pull determines the rate at which latent heat is released. Although the analysis is not a simple one, it is clear that to obtain an ingot with a large cross-sectional area, the pull speed must be slow. Typical growth rates are a few millimeters per minute.

The sizes and diameters of crystals grown by the Czochralski method are obviously limited by the equipment, though crystals 20–30 cm in diameter and 1–2 m in length are routinely grown for the IC fabrication industry. Also, the crystal orientation of the seed and its flatness with melt surface are important engineering requirements. For example, for very large scale integration (VLSI), the seed is placed with its (100) plane flat to the melt, so that the axis of the cylindrical ingot is along the [100] direction.

Following growth, the Si ingot is usually ground to a specified diameter. Using X-ray diffraction, the crystal orientation is identified and either a flat or an edge is ground along the ingot, as shown in Figure 1.56b. Subsequently, the ingot is cut into thin wafers by a rotating annular diamond saw. To remove any damage to the wafer surfaces caused by sawing and obtain flat, parallel surfaces, the wafers are lapped (ground flat with alumina powder and glycerine), chemically etched, and then polished. The wafers are then used in IC fabrication, usually as a substrate for the growth of a thin layer of crystal from the vapor phase.

The Czochralski technique is also used for growing Ge, GaAs, and InP single crystals, though each case has its own particular requirements. The main drawback of the Czochralski technique is that the final Si crystal inevitably contains oxygen impurities dissolved from the quartz crucible.

¹⁵ The induced eddy currents in the graphite give rise to I^2R heating of the graphite susceptor.

1.11 GLASSES AND AMORPHOUS SEMICONDUCTORS

1.11.1 GLASSES AND AMORPHOUS SOLIDS

A characteristic property of the crystal structure is its periodicity and degree of symmetry. For each atom, the number of neighbors and their exact orientations are well defined; otherwise, the periodicity would be lost. There is therefore a **long-range order** resulting from strict adherence to a well-defined bond length and **relative bond angle** (or exact orientation of neighbors). Figure 1.57a schematically illustrates the presence of a clear, long-range order in a hypothetical two-dimensional crystal. Taking an arbitrary origin, we can predict the position of each atom anywhere in the crystal. We can perhaps use this to represent crystalline SiO_2 (silicon dioxide), for example, in two dimensions. In reality, a Si atom bonds with four oxygen atoms to form a tetrahedron, and the tetrahedra are linked at the corners to create a three-dimensional crystal structure.

Not all solids exhibit crystallinity. Many substances exist in a noncrystalline or amorphous form, due to their method of formation. For example, SiO_2 can have an amorphous structure, as illustrated schematically in two dimensions in Figure 1.57b. In the amorphous phase, SiO_2 is called **vitreous silica**, a form of glass, which has wide engineering applications, including optical fibers. The structure shown in the figure for vitreous silica is essentially that of a frozen liquid, or a **supercooled liquid**. Vitreous silica is indeed readily obtained by cooling the melt.

Many amorphous solids are formed by rapidly cooling or quenching the liquid to temperatures where the atomic motions are so sluggish that crystallization is virtually halted. (The cooling rate is measured relative to the crystallization rate, which depends on atomic diffusion.) We refer to these solids as **glasses**. In the liquid state, the atoms

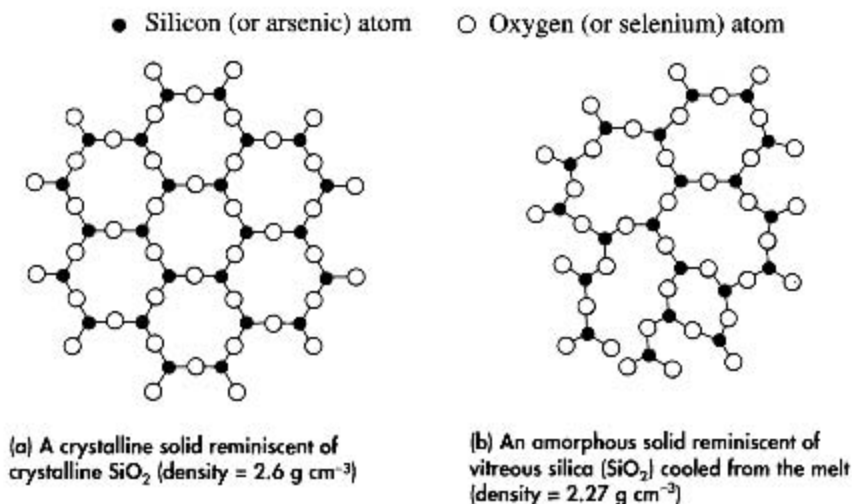


Figure 1.57 Crystalline and amorphous structures illustrated schematically in two dimensions.

have sufficient kinetic energy to break and make bonds frequently and to bend and twist their bonds. There are bond angle variations, as well as rotations of various atoms around bonds (**bond twisting**). Thus, the bonding geometry around each atom is not necessarily identical to that of other atoms, which leads to the loss of long-range order and the formation of an amorphous structure, as illustrated in Figure 1.57b for the same material in Figure 1.57a. We may view Figure 1.57b as a snapshot of the structure of a liquid. As we move away from a reference atom, after the first and perhaps the second neighbors, random bending and twisting of the bonds is sufficient to destroy long-range order. The amorphous structure therefore lacks the long-range order of the crystalline state.

To reach the glassy state, the temperature is rapidly dropped well below the melting temperature where the atomic diffusion processes needed for arranging the atoms into a crystalline structure are infinitely slow on the time scale of the observation. The liquid structure thus becomes frozen. Figure 1.57b shows that for an amorphous structure, the coordination of each atom is well defined, because each atom must satisfy its chemical bonding requirement, but the whole structure lacks long-range order. Therefore, there is only a **short-range order** in an amorphous solid. The structure is a **continuous random network** of atoms (often called a CRN model of an amorphous solid). As a consequence of the lack of long-range order, amorphous materials do not possess such crystalline imperfections as grain boundaries and dislocations, which is a distinct advantage in certain engineering applications.

Whether a liquid forms a glass or a crystal structure on cooling depends on a combination of factors, such as the nature of the chemical bond between the atoms or molecules, the viscosity of the liquid (which determines how easily the atoms move), the rate of cooling, and the temperature relative to the melting temperature. For example, the oxides SiO_2 , B_2O_3 , GeO_2 , and P_2O_5 have directional bonds that are a mixture of covalent and ionic bonds and the liquid is highly viscous. These oxides readily form glasses on cooling from the melt. On the other hand, it is virtually impossible to quench a pure metal, such as copper, from the melt, bypass crystallization, and form a glass. The metallic bonding is due to an electron gas permeating the space between the copper ions, and that bonding is nondirectional, which means that on cooling, copper ions are readily (and hence, quickly) shifted with respect to each other to form the crystal. There are, however, a number of metal-metal ($\text{Cu}_{66}\text{Zr}_{33}$) and metal-metalloid alloys ($\text{Fe}_{80}\text{B}_{20}$, $\text{Pd}_{80}\text{Si}_{20}$) that form glasses if quenched at ultrahigh cooling rates of 10^6 – 10^8 °C s^{-1} . In practice, such cooling rates are achieved by squirting a thin jet of the molten metal against a fast-rotating, cooled copper cylinder. On impact, the melt is frozen within a few milliseconds, producing a long ribbon of metallic glass. The process is known as **melt spinning** and is depicted in Figure 1.58.

Many solids used in various applications have an amorphous structure. The ordinary window glass (SiO_2)_{0.8}(Na_2O)_{0.2} and the majority of glassware are common examples. Vitreous silica (SiO_2) mixed with germania (GeO_2) is used extensively in optical fibers. The insulating oxide layer grown on the Si wafer during IC fabrication is the amorphous form of SiO_2 . Some intermetallic alloys, such as $\text{Fe}_{0.8}\text{B}_{0.2}$, can be rapidly quenched from the liquid (as shown in Figure 1.58) to obtain a glassy metal used in low-loss transformer cores. Arsenic triselenide, As_2Se_3 , has a crystal structure that resembles the two-dimensional sketch in Figure 1.57a, where an As atom (valency III) bonds with three Se atoms, and a Se atom (valency VI) bonds with two As atoms. In the amorphous

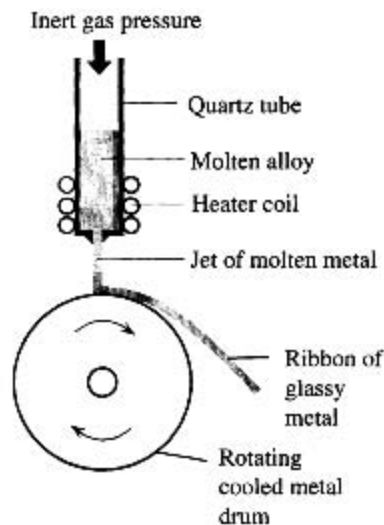
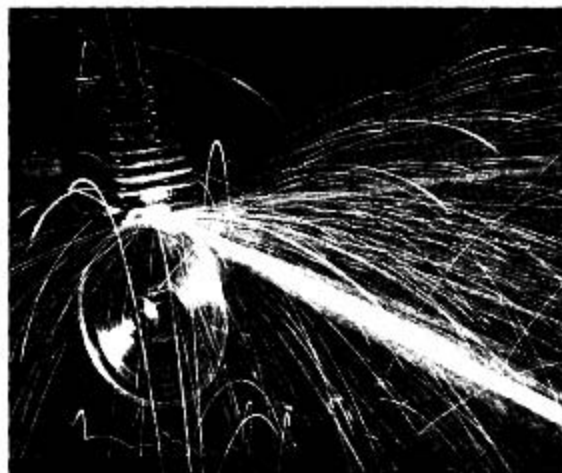


Figure 1.58 It is possible to rapidly quench a molten metallic alloy, thereby bypassing crystallization, and forming a glassy metal commonly called a metallic glass.

The process is called *melt spinning*.



Melt spinning involves squirting a jet of molten metal onto a rotating cool metal drum. The molten jet is instantly solidified into a glassy metal ribbon which is a few microns in thickness. The process produces roughly 1 to 2 kilometers of ribbon per minute.

! SOURCE: Photo courtesy of the Estate of Fritz Goro.

phase, this crystal structure looks like the sketch in Figure 1.57b, in which the bonding requirements are only locally satisfied. The crystal can be prepared by condensation from the vapor phase, or by cooling the melt. The vapor-grown films of amorphous As_2Se_3 are used in some photoconductor drums in the photocopying industry.

1.11.2 CRYSTALLINE AND AMORPHOUS SILICON

A silicon atom in the silicon crystal forms four tetrahedrally oriented, covalent bonds with four neighbors, and the repetition of this exact bonding geometry with a well-defined bond length and angle leads to the diamond structure shown in Figure 1.6. A simplified two-dimensional sketch of the Si crystal is shown in Figure 1.59. The crystal has a clear long-range order. Single crystals of Si are commercially grown by the Czochralski crystal pulling technique.

It is also possible to grow amorphous silicon, denoted by a-Si, by the condensation of Si vapor onto a solid surface, called a substrate. For example, an electron beam is used to vaporize a silicon target in a vacuum; the Si vapor then condenses on a metallic substrate to form a thin layer of solid noncrystalline silicon. The technique, which is schematically depicted in Figure 1.60, is referred to as **electron beam deposition**. The structure of amorphous Si (a-Si) lacks the long-range order of crystalline Si (c-Si), even though each Si atom in a-Si, on average, prefers to bond

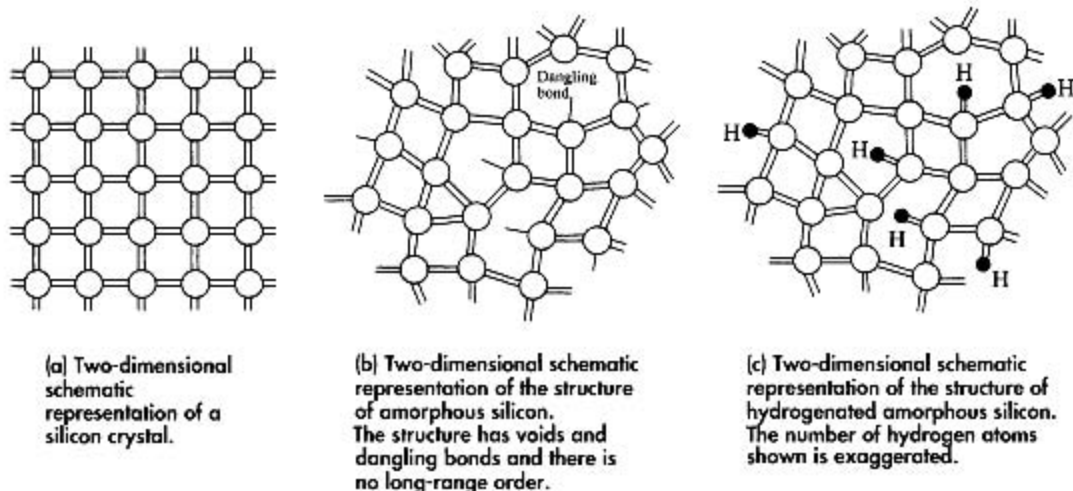


Figure 1.59 Silicon can be grown as a semiconductor crystal or as an amorphous semiconductor film. Each line represents an electron in a bond. A full covalent bond has two lines, and a broken bond has one line.

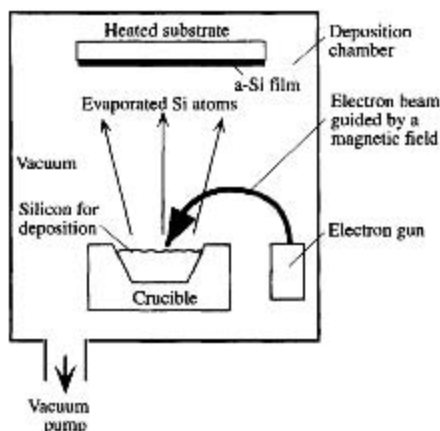


Figure 1.60 Amorphous silicon, a-Si, can be prepared by an electron beam evaporation of silicon.

Silicon has a high melting temperature, so an energetic electron beam is used to melt the crystal in the crucible locally and thereby vaporize Si atoms. Si atoms condense on a substrate placed above the crucible, to form a film of a-Si.

with four neighbors. The difference is that the relative angles between the Si-Si bonds in a-Si deviate considerably from those in the crystal, which obey a strict geometry. Therefore, as we move away from a reference atom in a-Si, eventually the periodicity for generating the crystalline structure is totally lost, as illustrated schematically in Figure 1.59. Furthermore, because the Si-Si bonds do not follow the equilibrium geometry, the bonds are strained and some are even missing, simply because the formation of a bond causes substantial bond bending. Consequently, the a-Si structure has many voids and incomplete bonds, or **dangling bonds**, as schematically depicted in Figure 1.59.

One way to reduce the density of dangling bonds is simply to terminate a dangling bond using hydrogen. Since hydrogen only has one electron, it can attach itself to a

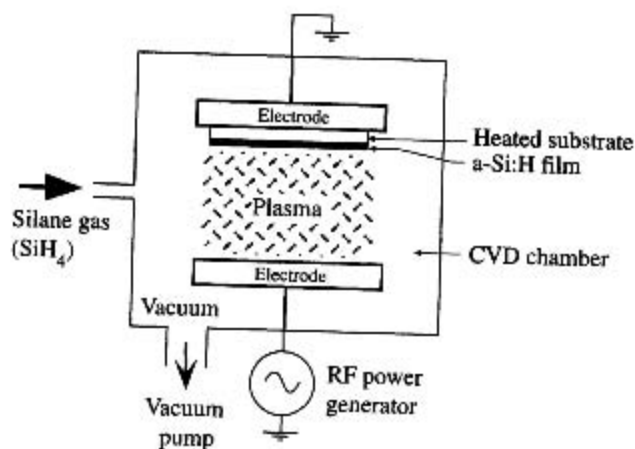


Figure 1.61 Hydrogenated amorphous silicon, a-Si:H, is generally prepared by the decomposition of silane molecules in a radio frequency (RF) plasma discharge. Si and H atoms condense on a substrate to form a film of a-Si:H.

dangling bond, that is, passivate the dangling bond. The structure resulting from hydrogen in amorphous silicon is called **hydrogenated amorphous Si (a-Si:H)**.

Many electronic devices, such as a-Si:H solar cells, are based on a-Si being deposited with H to obtain a-Si:H, in which the hydrogen concentration is typically 10 at. % (atomic %). The process involves the decomposition of silane gas, SiH₄, in an electrical plasma in a vacuum chamber. Called **plasma-enhanced chemical vapor deposition (PECVD)**, the process is illustrated schematically in Figure 1.61. The silane gas molecules are dissociated in the plasma, and the Si and H atoms then condense onto a substrate to form a film of a-Si:H. If the substrate temperature is too hot, the atoms on the substrate surface will have sufficient kinetic energy, and hence the atomic mobility, to orient themselves to form a polycrystalline structure. Typically, the substrate temperature is ~250 °C. The advantage of a-Si:H is that it can be grown on large areas, for such applications as photovoltaic cells, flat panel thin-film transistor (TFT) displays, and the photoconductor drums used in some photocopying machines. Table 1.5 summarizes the properties of crystalline and amorphous silicon, in terms of structure and applications.

Table 1.5 Crystalline and amorphous silicon

	Crystalline Si (c-Si)	Amorphous Si (a-Si)	Hydrogenated a-Si (a-Si:H)
Structure	Diamond cubic.	Short-range order only. On average, each Si covalently bonds with four Si atoms. Has microvoids and dangling bonds.	Short-range order only. Structure typically contains 10% H. Hydrogen atoms passivate dangling bonds and relieve strain from bonds.
Typical preparation	Czochralski technique.	Electron beam evaporation of Si.	Chemical vapor deposition of silane gas by RF plasma.
Density (g cm ⁻³)	2.33	About 3–10% less dense.	About 1–3% less dense.
Electronic applications	Discrete and integrated electronic devices.	None	Large-area electronic devices such as solar cells, flat panel displays, and some photoconductor drums used in photocopying.

1.12 SOLID SOLUTIONS AND TWO-PHASE SOLIDS

1.12.1 ISOMORPHOUS SOLID SOLUTIONS: ISOMORPHOUS ALLOYS

A **phase** of a material has the same composition, structure, and properties everywhere, so it is a homogeneous portion of the chemical system under consideration. In a given chemical system, one phase may be in contact with another phase. For example, at 0 °C, iced water will have solid and liquid phases in contact. Each phase, ice and water, has a distinct structure.

A bartender knows that alcohol and water are totally miscible; she can dilute whisky with as much water as she likes. When the two liquids are mixed, the molecules are randomly mixed with each other and the whole liquid is a homogeneous mixture of the molecules. The liquid therefore has one phase; the properties of the liquid are the same everywhere. The same is not true when we try to mix water and oil. The mixture consists of two distinctly separate phases, oil and water, in contact. Each phase has a different composition, even though both are liquids.

Many solids are a homogeneous mixture of two types of separate atoms. For example, when nickel atoms are added to copper, Ni atoms substitute directly for the Cu atoms, and the resulting solid is a **solid solution**, as depicted in Figure 1.62a. The structure remains an FCC crystal whatever the amount of Ni we add, from 100% Cu to 100% Ni. The solid is a homogeneous mixture of Cu and Ni atoms, with the same structure everywhere in the solid solution, which is called an **isomorphous solid solution**. The atoms in the majority make up the **solvent**, whereas the atoms in the minority are the **solute**, which is dissolved in the solvent. For a Cu–Ni alloy with a Ni content of less than 50 at.%, copper is the solvent and nickel is the solute.

The substitution of solute atoms for solvent atoms at various lattice sites of the solvent can be either random (disordered) or ordered. The two cases are schematically illustrated in Figure 1.62a and b, respectively. In many solid solutions, the substitution is random, but for certain compositions, the substitution becomes ordered. There is a

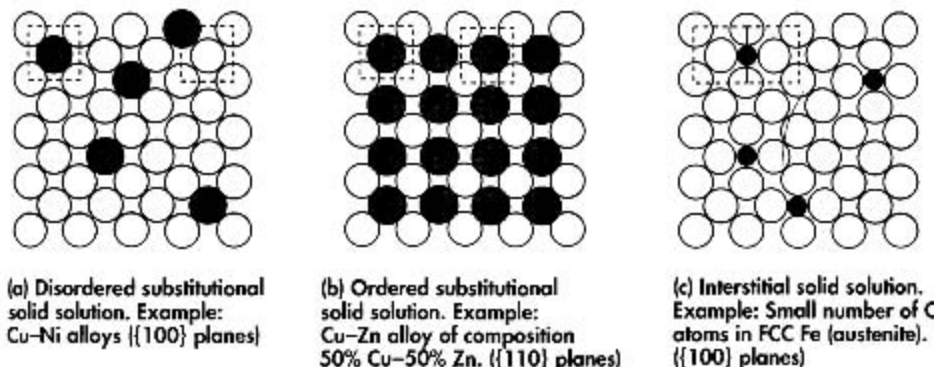


Figure 1.62 Solid solutions can be disordered substitutional, ordered substitutional, and interstitial substitutional.

Only one phase within the alloy has the same composition, structure, and properties everywhere.

distinct ordering of atoms around each solute atom such that the crystal structure resembles that of a compound. For example, β' brass has the composition 50 at.% Cu–50 at.% Zn. Each Zn atom is surrounded by eight Cu atoms and vice versa, as depicted in two dimensions in Figure 1.62b. The structure is that of a metallic compound between Cu and Zn.

Another type of solid solution is the **interstitial solid solution**, in which solute atoms occupy interstitial sites, or voids between atoms, in the crystal. Figure 1.62c shows an example in which a small number of carbon atoms have been dissolved in a γ -iron crystal (FCC) at high temperatures.

1.12.2 PHASE DIAGRAMS: Cu–Ni AND OTHER ISOMORPHOUS ALLOYS

The Cu–Ni alloy is isomorphous. Unlike pure copper or pure nickel, when a Cu–Ni alloy melts, its melting temperature is not well defined. The alloy melts over a range of temperatures in which both the liquid and the solid coexist as a heterogeneous mixture. It is therefore instructive to know the phases that exist in a chemical system at various temperatures as a function of composition, and this need leads to the use of phase diagrams.

Suppose we take a crucible of molten copper and allow it to cool. Above its melting temperature (1083 °C), there is only the liquid phase. The temperature drops with time, as shown in Figure 1.63a, until at the melting or fusion temperature at point L_0 when copper crystals begin to **nucleate** (solidify) in the crucible. During solidification, the temperature remains constant. As long as we have both the liquid and solid phases coexisting, the temperature remains constant at 1083 °C. During this time, heat is given off as the Cu atoms in the melt attach themselves to the Cu crystals. This heat is called the **heat of fusion**. Once all the liquid has solidified (point S_0), the temperature begins to drop as the solid cools. There is therefore a sharp melting temperature for copper, at 1083 °C.

If we were to cool pure nickel from its melt, we would observe a behavior similar to that of pure copper, with a well-defined melting temperature at 1453 °C.

Now suppose we cool the melt of a Cu–Ni alloy with a composition¹⁶ of 80 wt.% Cu and 20 wt.% Ni. In the melt, the two species of atoms are totally miscible, and there is only a single liquid phase. As the cooling proceeds, we reach the temperature 1195 °C, identified as point L_{20} in Figure 1.63a, where the first crystals of Cu–Ni alloy begin to appear. In this case, however, the temperature does not remain constant until the liquid is solidified, but continues to drop. Thus, there is no single melting temperature, but a range of temperatures over which both the liquid and the solid phases coexist in a heterogeneous mixture. We find that when the temperature reaches 1130 °C, corresponding to point S_{20} , all the liquid has solidified. Below 1130 °C, we have a single-phase solid that is an isomorphous solid solution of Cu and Ni. If we repeat these experiments for other compositions, we find a similar behavior; that is, freezing occurs over a transition temperature range. The beginning and end

¹⁶In materials science, we generally prefer to give alloy composition in wt.%, which henceforth will simply be %.

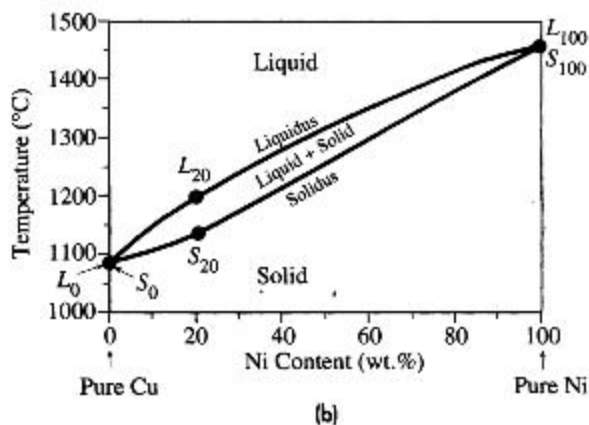
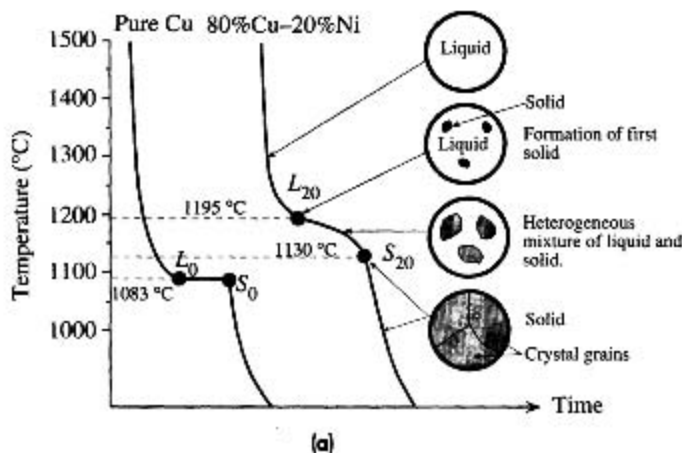


Figure 1.63 Solidification of an isomorphous alloy such as Cu–Ni.

(a) Typical cooling curves.

(b) The phase diagram marking the regions of existence for the phases.

of solidification, at points L and S , respectively, depend on the specific composition of the alloy.

To characterize the freezing or melting behavior of other compositions of Cu–Ni alloys, we can plot the temperatures for the beginning and end of solidification versus the composition and identify those temperature regions where various phases exist, as shown in Figure 1.63b. When we join all the points corresponding to the beginning of freezing, that is, all the L points, we obtain what is called the **liquidus curve**. For any given composition, only the liquid phase can exist above the liquidus curve. If we join all the points where the liquid has totally solidified, that is, all the S points, we have a curve called the **solidus curve**. At any temperature and composition below the solidus curve, we can only have the solid phase. The region between

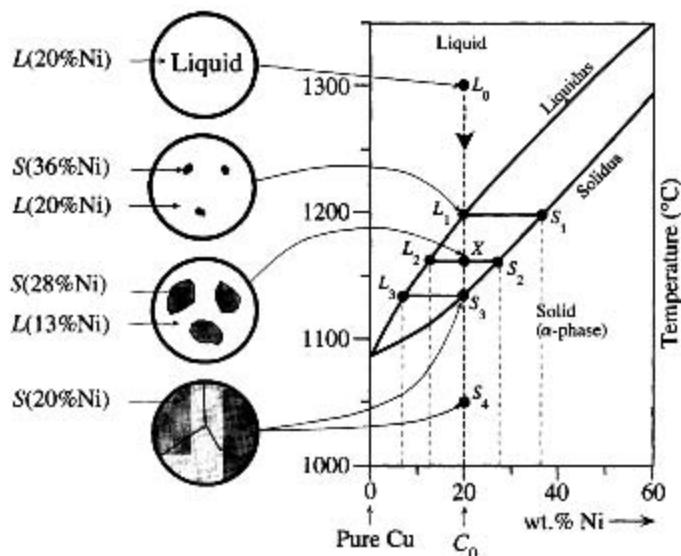


Figure 1.64 Cooling of a 80% Cu–20% Ni alloy from the melt to the solid state.

the liquidus and solidus curves marks where a heterogeneous mixture of liquid and solid phases exists.

Let's follow the cooling behavior of the 80% Cu–20% Ni alloy from the melt at 1300 °C down to the solid state at 1000 °C, as shown in Figure 1.64. The vertical dashed line at 20% Ni represents the overall composition of the alloy (the whole chemical system) and the cooling process corresponds to movement down this dashed line, starting from the liquid phase at L_0 .

When the Cu–Ni alloy begins to solidify at 1195 °C, at point L_1 , the first solid that forms is richer in Ni content. The only solid that can exist at this temperature has a composition S_1 , which has a greater Ni content than the liquid, as shown in Figure 1.64. Intuitively, we can see this by noting that Cu, the component with the lower melting temperature, prefers to remain in the liquid, whereas Ni, which has a higher melting temperature, prefers to remain in the solid. When the temperature drops further, say to 1160 °C (indicated by X in the figure), the alloy is a heterogeneous mixture of liquid and solid. At this temperature, the only solid that can coexist with the liquid has a composition S_2 . The liquid has the composition L_2 . Since the liquid has lost some of its Ni atoms, the liquid composition is less than that at L_1 . The liquidus and solidus curves therefore give the compositions of the liquid and solid phases coexisting in the heterogeneous mixture during melting.

At 1160 °C, the overall composition of the alloy (the whole chemical system) is still 20% Ni and is represented by point X in the phase diagram. When the temperature reaches 1130 °C, nearly all the liquid has been solidified. The solid has the composition S_3 , which is 20% Ni, as we expect since the whole alloy is almost all solid. The last drops of the liquid in the alloy have the composition L_3 , since at this temperature,

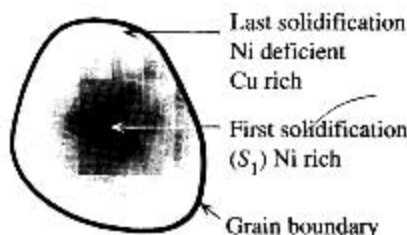
Table 1.6 Phase in the 80% Cu–20% Ni isomorphous alloy

Temperature, °C	Phases	Composition	Amount
1300	Liquid only	$L_0 = 20\% \text{ Ni}$	100%
1195	Liquid and solid	$L_1 = 20\% \text{ Ni}$ $S_1 = 36\% \text{ Ni}$	100% First solid appears
1160	Liquid and solid	$L_2 = 13\% \text{ Ni}$ $S_2 = 28\% \text{ Ni}$	53.3% 46.7%
1130	Liquid and solid	$L_3 = 7\% \text{ Ni}$ $S_3 = 20\% \text{ Ni}$	The last liquid drop 100%
1050	Solid only	$S_4 = 20\% \text{ Ni}$	100%

only the liquid with this composition can coexist with the solid at S_3 . Table 1.6 summarizes the phases and their compositions, as observed during the cooling process depicted in Figure 1.64. By convention, all solid phases that can exist are labeled by different Greek letters. Since we can only have one solid phase, this is labeled the α -phase.

During the solidification process depicted in Figure 1.64, the solid composition changes from S_1 to S_2 to S_3 . We tacitly assume that the cooling is sufficiently slow to allow time for atomic diffusion to change the composition of the whole solid. Therefore, the phase diagram in Figure 1.63b, which assumes near equilibrium conditions during cooling, is termed an **equilibrium phase diagram**. If the cooling is fast, there will be limited time for atomic diffusion in the solid phase, and the resulting solid will have a composition variation. The inner core will correspond to the solidification at S_1 and will be Ni rich. Since the solidification occurs quickly, the Ni atoms do not have time to diffuse out from the inner core to allow the composition in the solid to change from S_1 to S_2 to S_3 . Thus, the outer region, the final solidification, will be Ni deficient (or Cu rich); its composition is not S_3 but less, because S_3 is the average composition in the whole solid. The solid structure will be **cored**, as depicted in Figure 1.65. The cooling process is then said to have occurred under nonequilibrium conditions, which leads to a segregation of the elements in the grains. Under nonequilibrium cooling conditions we cannot quantitatively use the equilibrium phase diagram in Figure 1.63b. The diagram can only serve as a qualitative guide.

The amounts of liquid and solid in the mixture can be determined from the phase diagram using the **lever rule**, which is based on the fact that the total mass of the alloy

**Figure 1.65** Segregation in a grain due to rapid cooling [nonequilibrium cooling].

remains the same throughout the entire cooling process. Let W_L and W_S be the **weight (or mass) fraction** of the liquid and solid phases in the alloy mixture. The compositions of the liquid and solid are denoted as C_L and C_S , respectively. The overall composition of the alloy is denoted C_O , which is the overall weight fraction of Ni in the alloy.

If we take the alloy to have a weight of unity, then the conservation of mass means that

$$W_L + W_S = 1$$

Further, the weight fraction of Ni in both the liquid and solid must add up to the composition C_O of Ni in the whole alloy, or

$$C_L W_L + C_S W_S = C_O$$

We can substitute for W_S in the above equation to find the weight fraction of the liquid and then that of the solid phase, as follows:

Lever rules

$$W_L = \frac{C_S - C_O}{C_S - C_L} \quad \text{and} \quad W_S = \frac{C_O - C_L}{C_S - C_L} \quad [1.36]$$

To apply Equation 1.36, we first draw a line (called a **tie line**) from L_2 to S_2 corresponding to C_L and C_S , as shown in Figure 1.64. The line represents a “horizontal lever” and point X at C_O at this temperature is the lever’s fulcrum. The lengths of the lever arms from the fulcrum to the liquidus and solidus curves are $(C_O - C_L)$ and $(C_S - C_O)$, respectively. The lever must be balanced by the weights W_L and W_S attached to the ends. The total length of the lever is $(C_S - C_L)$. At 1160 °C, $C_L = 0.13$ (13% Ni) and $C_S = 0.28$ (28% Ni), so the weight fraction of the liquid phase is

$$W_L = \frac{C_S - C_O}{C_S - C_L} = \frac{0.28 - 0.20}{0.28 - 0.13} = 0.533 \quad \text{or} \quad 53.3\%$$

Similarly, the weight fraction of the solid phase is $1 - 0.533$ or 0.467.

1.123 ZONE REFINING AND PURE SILICON CRYSTALS

Zone refining is used for the production of high-purity crystals. Silicon, for example, has a high melting temperature, so any impurities present in the crystal decrease the melting temperature. This is similar to the depression of the melting temperature of pure Ni by the addition of Cu, as shown by the right-hand side of Figure 1.63b. We can represent the phase diagram of Si with small impurities as shown in Figure 1.66. Consider what happens if we have a rod of the solid and we melt only the left end by applying heat locally (using RF heating, for example). At the same time, we move the melted zone toward the right by moving the heater. We therefore melt the solid at A and refreeze it at B , as shown in Figure 1.67a.

The solid has an impurity concentration of C_O ; when it melts at A , the melt initially also has the same concentration $C_L = C_O$. However, at temperature T_B , the melt

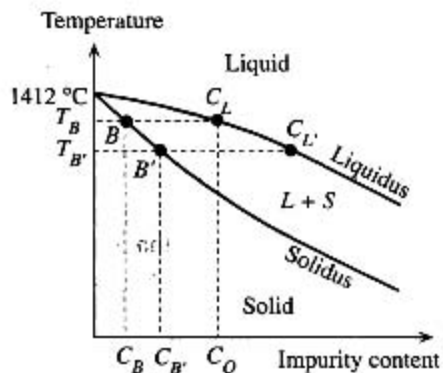
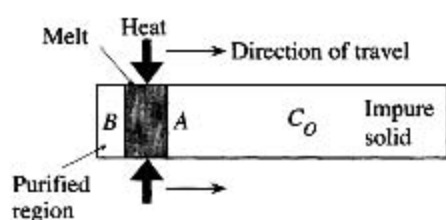
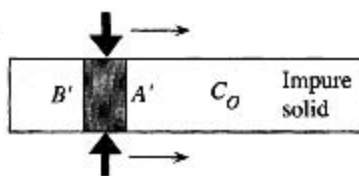


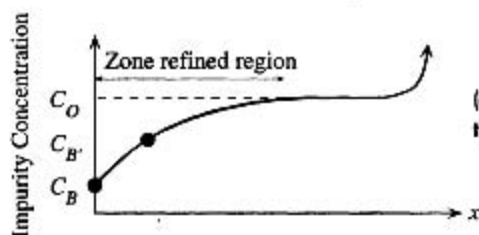
Figure 1.66 The phase diagram of Si with impurities near the low-concentration region.



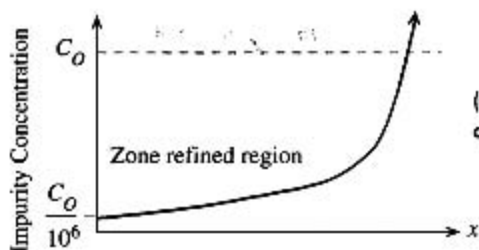
(a) Heat is applied locally starting at one end. The impurity concentration in the refrozen solid at B is $C_B < C_0$. The impurity concentration in the melt is $C_L' > C_0$.



(b) As the torch travels toward the right, the refrozen solid at B' has $C_{B'}$ where $C_B < C_{B'} < C_0$. The impurity concentration in the melt is now even greater than C_L' .



(c) The impurity concentration profile in the refrozen solid after one pass.



(d) Typical impurity concentration profile after many passes.

Figure 1.67 The principle of zone refining.

begins to solidify. At the start of solidification the solid that freezes has a composition C_B , which is considerably less than C_0 , as is apparent in Figure 1.66. The cooling at B occurs rapidly, so the concentration C_B cannot adjust to the equilibrium value at the end of freezing. Thus, the solid that freezes at B has a lower concentration of impurities. The impurities have been pushed out of the solid at B and into the melt, whose impurity concentration increases from C_L to C_L' .

Next, refreezing at B' , shown in Figure 1.67b, occurs at a lower temperature $T_{B'}$, because the melt concentration C_L is now greater than C_0 . The solid that freezes at B' has the concentration $C_{B'}$, shown in Figure 1.66, which is greater than C_B but less than C_0 . As the melted zone is floated toward the right, the melt that is solidified at $B, B',$ etc., has a higher and higher impurity concentration, until its impurity content reaches that of the impure solid, at which point the concentration remains at C_0 . When the melted zone approaches the far right where the freezing is halted, the impurities in the final melt appear in the last frozen region at the far right. The resulting impurity concentration profile is schematically depicted in Figure 1.67c. The region of impurity concentration below C_0 is the **zone refined** section of the rod. The zone refining procedure can be repeated again, starting from the left toward the right, to reduce the impurity concentration even lower. The impurity concentration profile after many passes is sketched in Figure 1.67d. Although the profile is nonuniform, due to the segregation effect, the impurity concentrations in the zone refined section may be as low as a factor of 10^{-6} .

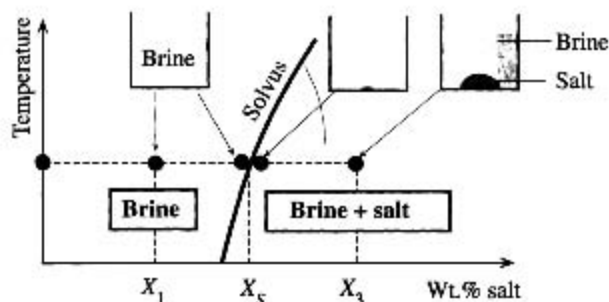
1.12.4 BINARY EUTECTIC PHASE DIAGRAMS AND Pb–Sn SOLDERS

When we dissolve salt in water, we obtain a brine solution. If we continue to add more salt, we eventually reach the solubility limit of salt in the solution, and the excess salt remains as a solid at the bottom of the container. We then have two coexisting phases: brine (liquid solution) and salt (solid), as shown in Figure 1.68. The solubility limit of one component in another in a mixture is represented by a **solvus curve** shown schematically in Figure 1.68 for salt in brine. In the solid state, there are many elements that can only be dissolved in small amounts in another solid.

Lead in the solid phase has an FCC crystal structure, and tin has a BCT (body-centered tetragonal) structure. Although the two elements are totally miscible in any

Figure 1.68 We can only dissolve so much salt in brine (solution of salt in water).

Eventually we reach the solubility limit at X_S , which depends on the temperature. If we add more salt, then the excess salt does not dissolve and coexists with the brine. Past X_S we have two phases, brine (solution) and salt (solid).



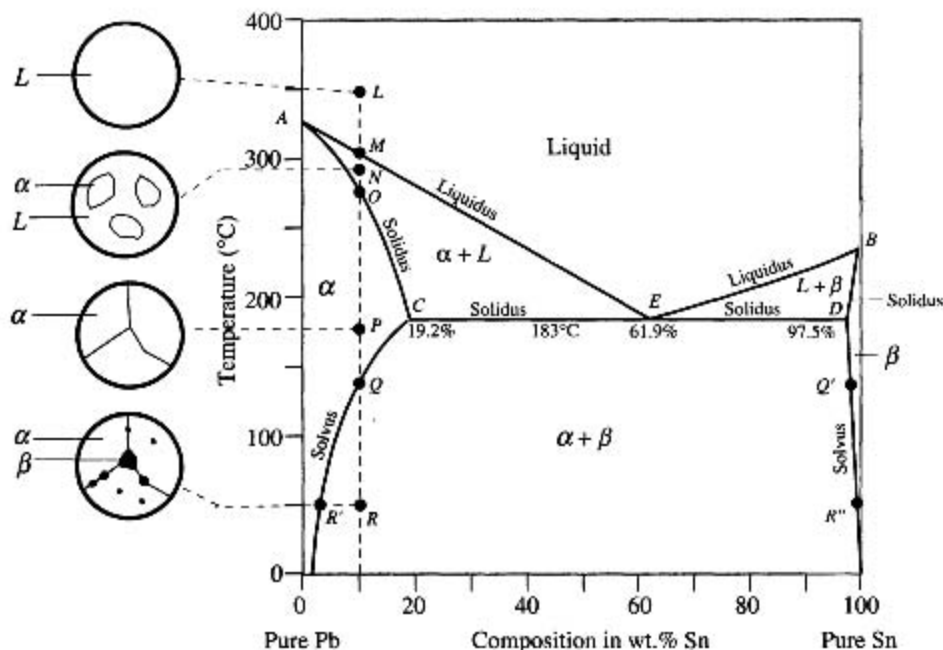


Figure 1.69 The equilibrium phase diagram of the Pb–Sn alloy.

The microstructures on the left show the observations at various points during the cooling of a 90% Pb–10% Sn from the melt along the dashed line (the overall alloy composition remains constant at 10% Sn).

proportion when melted, this is not so in the solid state. We can only dissolve so much Sn in solid Pb, and vice versa. We quickly reach the solubility limit, and the resulting solid is a mixture of two distinctly different solid phases. One solid phase, labeled α , is Pb rich and has the FCC structure with some Sn atoms dissolved in the crystal. The amount of Sn dissolved in α is given by the solvus curve of Sn in α at that temperature. The other phase, labeled β , is Sn rich and has the BCT structure with some Pb atoms dissolved in it. The amount of Pb dissolved in β is given by the solvus curve of Pb in β at that temperature.

The existence of various phases and their compositions as a function of temperature are given by the equilibrium phase diagram for the Pb–Sn alloy, shown in Figure 1.69. This is called an equilibrium **eutectic phase diagram**. The liquidus and solidus curves, as usual, mark the borders for the liquid and solid phases. Between the liquidus and solidus curves, we have a heterogeneous mixture of melt and solid. Unlike the Cu–Ni case, the melting temperature of both elements here is depressed with alloying. The liquidus and solidus curves thus decrease from both ends, starting at A and B. They meet at a point E, called the **eutectic point**, at 61.9% Sn and 183 °C. This point has a special significance: No liquid can exist below this temperature, so 183 °C is the lowest melting temperature of the alloy.

In addition, we must insert the solvus curves at both the Pb and Sn ends to mark the extent of solid-state solubility and hence identify the two-phase solid region. The solvus curve for the solubility limit of Sn in Pb meets the solidus curve at point *C*, 19.2% Sn. Similarly, the solubility limit of Pb in Sn meets the solvus curve at *D*. A characteristic feature of this phase diagram is that *CD* is a straight line through *E* at 183 °C. Below 183 °C, between the two solvus curves, we have a solid with two phases, α and β . This is identified as $\alpha + \beta$ in the diagram.

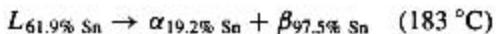
The usefulness of such a phase diagram is best understood by examining the phase transformations and microstructures during the cooling of a melt of a given composition alloy. Consider a 90% Pb–10% Sn alloy being cooled from the melt at 350 °C (point *L*) where there is only one phase, the liquid phase. At point *M*, 315 °C, few nuclei of the α -phase appear in the liquid. The composition of the α -phase is given by the solidus curve at 315 °C and is about 5% Sn. At point *N*, 290 °C, there is more α -phase in the mixture. The compositions of the liquid and α -phases are given respectively by the liquidus and solidus curves at 290 °C. At point *O*, 275 °C, all liquid has been solidified into the α -phase, which then has the composition 10% Sn.

Between *M* and *O*, the alloy is a coexistent mixture of the liquid phase (melt) and the solid α -phase. At point *P*, 175 °C, we still have only the α -phase. When we reach the solvus curve at point *Q*, 140 °C, we can no longer keep all the Sn dissolved in the α -phase, as we have reached the solubility limit of Sn in α . Some of the Sn atoms must diffuse out from the α -phase; they do so by forming a second solid phase, which is the β -phase. The β -phase nucleates within the α -phase (usually at the grain boundaries, where atomic diffusion occurs readily). The β -phase will contain as much dissolved Pb as is allowed by the solubility of Pb in the β -phase, which is given by the solvus curve on the Sn side and marked as point *Q'*, about 98% Sn. Thus, the microstructure is now a mixture of the α and β phases.

As cooling proceeds, the two phases continue to coexist, but their relative proportions change. At *R*, 50 °C, the alloy is a mixture of the α -phase given by *R'* (4% Sn) and the β -phase given by *R''* (99% Sn). The relative amounts of α and β phases are given by the lever rule. Figure 1.69 illustrates the microstructure of the 90% Pb–10% Sn alloy as it is cooled.

An interesting phenomenon can be observed when we cool an alloy of the eutectic composition 38.1% Pb–61.9% Sn from the melt. The cooling process and the observed microstructures are illustrated in Figure 1.70; the microstructures are on the right. The temperature–time profile is also depicted in Figure 1.70. At point *L*, 350 °C, the alloy is all liquid; as it cools, its temperature drops until point *E* at 183 °C. At *E*, the temperature remains constant and a solid phase nucleates within the melt. With time, the amount of solid grows until all the liquid is solidified and the temperature begins to drop again. This behavior is much like that of a pure element, for which melting occurs at a well-defined temperature. This behavior only occurs for the eutectic composition (61.9% Sn), because this is the composition at which the liquidus and solidus curves meet at one temperature. Generally, the liquid with the eutectic composition will solidify through the **eutectic transformation** at the eutectic temperature, or

Eutectic transformation



[1.37]

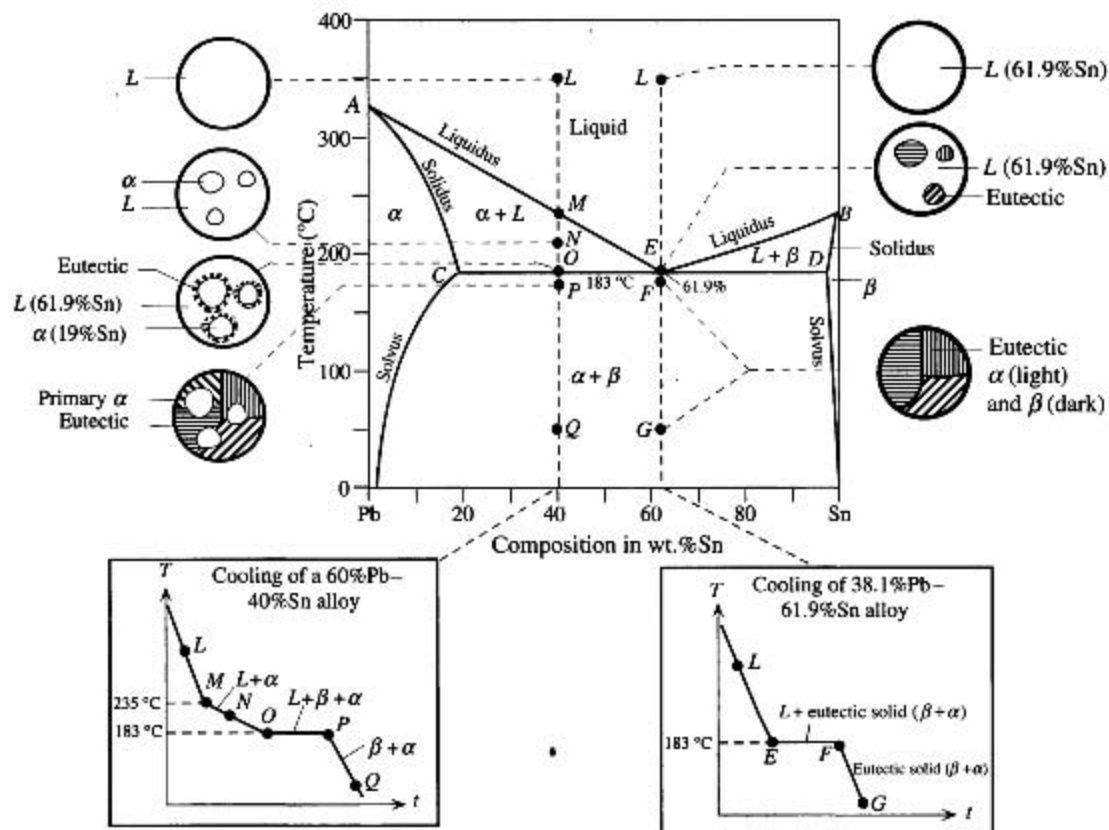


Figure 1.70 The alloy with the eutectic composition cools like a pure element, exhibiting a single solidification temperature at 183 °C.

The solid has the special eutectic structure. The alloy with the composition 60% Pb–40% Sn when solidified is a mixture of primary α and eutectic solid.

The solid that forms from the eutectic solidification has a special microstructure, consisting of alternating plates, or **lamellae**, of α and β phases, as shown in Figure 1.70. This is called the **eutectic microstructure** (or **eutectic solid**). The formation of a Pb-rich α -phase and an Sn-rich β -phase from the 61.9% Sn liquid requires the redistribution of the two types of atoms by atomic diffusion. Atomic diffusions are easier in the liquid than in the solid. The formation of a solid with alternating α and β layers allows the Pb and Sn atoms to diffuse in the liquid without having to move over long distances. The eutectic structure is not a phase itself, but a mixture of the two phases, α and β .

When cooled from the melt, an alloy with a composition between 19.2% Sn and 61.9% Sn solidifies into a mixture of α -phase and a eutectic solid (a mixture of α and β phases). Consider the cooling of an alloy with a composition of 40% Sn, starting from the liquid phase L at 350 °C, as shown in Figure 1.70. At point M (235 °C), the

first solid, the α -phase, nucleates. Its composition is about 15% Sn. At N , 210°C , the alloy is a mixture of liquid, composition 50% Sn, and α -phase, composition 18% Sn. The composition of the liquid thus moves along the liquidus line from M toward E . At 183°C , the liquid has the composition 61.9% Sn, or the eutectic composition, and therefore undergoes the eutectic transformation indicated in Equation 1.37. There is still α -phase in the alloy, but its composition is now 19.2% Sn; it does not take part in the eutectic transformation of the liquid. During the eutectic transformation, the temperature remains constant. When all the liquid has been solidified, we have a mixture of the preexisting α -phase, called **primary α** (or **proeutectic α**), and the newly formed eutectic solid. The final microstructure is shown in Figure 1.70 and consists of a primary α and a eutectic solid; therefore, two solid phases, α and β , coexist.

During cooling between points M and O , the alloy 60% Pb–40% Sn is a mixture of melt and α -phase, and it exhibits plastic-like characteristics while solidifying. Further, the temperature range for the solidification is about 183°C to 235°C , or about 50°C . Such an alloy is preferable for such uses as soldering wiped joints to join pipes together, giving the plumber sufficient play for adjusting and wiping the joint. On the other hand, a solder with the eutectic composition (commercially, this is 40% Pb–60% Sn solder, which is close to the eutectic) has the lowest melting temperature and solidifies quickly. The liquid also has good wetting properties. Therefore, 40% Pb–60% Sn is widely used for soldering semiconductor devices, where good wetting and minimal exposure to high temperature are required.

EXAMPLE 1.17

THE 60% Pb–40% Sn ALLOY Consider the solidification of the 60% Pb–40% Sn alloy. What are the phases, compositions, and weight fractions of various phases existing in the alloy at 250°C , 210°C , 183.5°C (just above 183°C), and 182.5°C (just below 183°C)?

SOLUTION

We again refer to the phase diagram in Figure 1.70 to identify which phases exist at what temperatures. At 250°C , we only have the liquid phase. At 210°C , point N , the liquid and the α -phase are in equilibrium. The composition of the α -phase is given by the solidus line; at 210°C , $C_\alpha = 18\%$ Sn. The composition of the liquid is given by the liquidus line; at 210°C , $C_L = 50\%$ Sn. To find the weight fraction of α the alloy, we use the lever rule,

$$W_\alpha = \frac{C_L - C_O}{C_L - C_\alpha} = \frac{50 - 40}{50 - 18} = 0.313$$

From $W_\alpha + W_L = 1$, we obtain the weight fraction of the liquid phase, $W_L = 1 - 0.313 = 0.687$.

At 183.5°C , point O , the composition of the α -phase is 19.2% Sn corresponding to C and that of the liquid is 61.9% Sn corresponding to E . The liquid therefore has the eutectic composition. The weight fractions are

$$W_\alpha = \frac{C_L - C_O}{C_L - C_\alpha} = \frac{61.9 - 40}{61.9 - 19.2} = 0.513$$

$$W_L = 1 - 0.513 = 0.487$$

As expected, the amount of α -phase increases during solidification; at the same time, its composition changes along the solidus curve. Just above 183°C , about half the alloy is the solid α -phase and the other half is liquid with the eutectic composition. Thus, on solidification, the liquid

Table 1.7 The 60% Pb–40% Sn alloy

Temperature (°C)	Phases	Composition	Mass (g)	Microstructure and Comment
250	<i>L</i>	40% Sn	100	
235	<i>L</i> α	40% Sn 15% Sn	100 0	The first solid (α -phase) nucleates in the liquid.
210	<i>L</i> α	50% Sn 18% Sn	68.7 31.3	Mixture of liquid and α phases. More solid forms. Compositions change.
183.5	<i>L</i> α	61.9% Sn 19.2% Sn	48.7 51.3	Liquid has the eutectic composition.
182.5	α β	19.2% Sn 97.5% Sn	73.4 26.6	Eutectic (α and β phases) and primary α -phase.

† Assume mass of the alloy is 100 g.

undergoes the eutectic transformation and forms the eutectic solid. Just below 183 °C, therefore, the microstructure is the primary α -phase and the eutectic solid. Stated differently, below 183 °C, the α and β phases coexist, and β is in the eutectic structure. The weight fraction of the eutectic phase is the same as that of the liquid just above 183 °C, from which it was formed. The weight fractions of α and β in the whole alloy are given by the lever rule applied at point *P*, or

$$W_{\alpha} = \frac{C_{\beta} - C_0}{C_{\beta} - C_{\alpha}} = \frac{97.5 - 40}{97.5 - 19.2} = 0.734$$

$$W_{\beta} = \frac{C_0 - C_{\alpha}}{C_{\beta} - C_{\alpha}} = \frac{40 - 19.2}{97.5 - 19.2} = 0.266$$

The microstructure at room temperature will be much like that just below 183 °C, at which the alloy is a two phase solid because atomic diffusions in the solid will not be sufficiently fast to allow the compositions to change. Table 1.7 summarizes the phases that exist in this alloy at various temperatures.

ADDITIONAL TOPICS

1.13 BRAVAIS LATTICES

An infinite periodic array of geometric points in space defines a **space lattice** or simply a **lattice**. Strictly, a lattice does not contain any atoms or molecules because it is simply an imaginary array of geometric points. A two-dimensional *simple square* lattice is shown in Figure 1.71a. In three dimensions, Figure 1.71a would correspond to the simple cubic (SC) lattice. The actual crystal is obtained from the lattice by placing an identical group of atoms (or molecules) at each lattice point. The identical group of atoms is called the **basis** of the crystal structure. Thus, conceptually, as illustrated in Figure 1.71a to c,

$$\text{Crystal} = \text{Lattice} + \text{Basis}$$

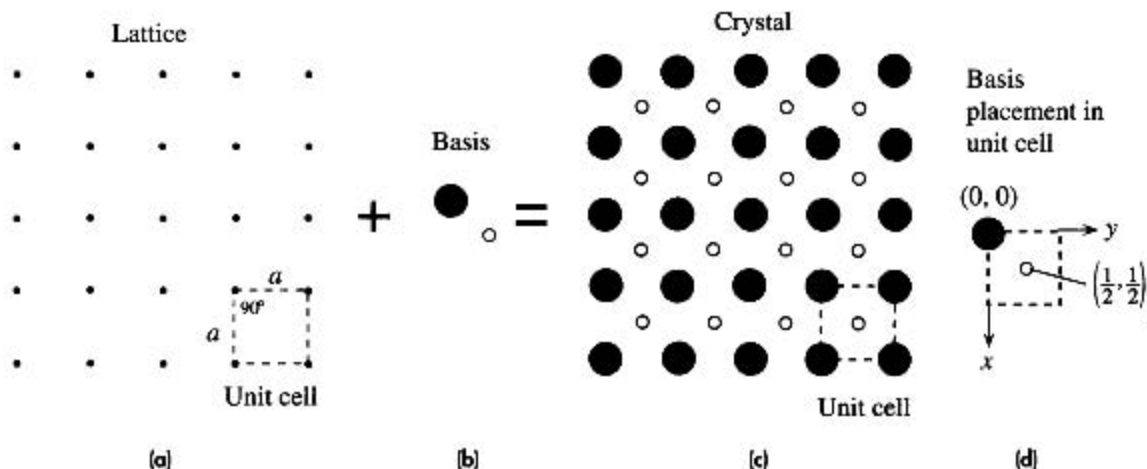


Figure 1.71

- (a) A simple square lattice. The unit cell is a square with a side a .
 (b) Basis has two atoms.
 (c) Crystal = Lattice + Basis. The unit cell is a simple square with two atoms.
 (d) Placement of basis atoms in the crystal unit cell.

The unit cell of the two-dimensional lattice in Figure 1.71a is a square which is characterized by the length a of one of the sides; a is called a **lattice parameter**. A given lattice can generate different *patterns* of atoms depending on the basis. The lattice in Figure 1.71a with the two-atom basis in Figure 1.71b produces the crystal in Figure 1.71c. Although the latter crystal appears as a body-centered square (similar to BCC in three dimensions), it is nonetheless a *simple square lattice* with two atoms comprising the basis. Suppose that the basis had only one atom; then the crystal would appear as the simple square lattice in Figure 1.71a (with each point now being an atom). The *patterns* in Figure 1.71a and c are different but the underlying lattice is the same. Because they have the same lattice, the two crystals would have certain identical symmetries. For example, for both crystals, a rotation by 90° about a lattice point would produce the same crystal structure.

To fully characterize the crystal, we also have to specify the locations of the basis atoms in the unit cell as in Figure 1.71d. By convention, we place a Cartesian coordinate system at the rear-left corner of the unit cell with the x and y axes along the square edges. We indicate the coordinates (x_i, y_i) of each i th atom in terms of the lattice parameters along x and y . Thus, the atoms in the unit cell in Figure 1.71d are at $(0, 0)$ and at $(\frac{1}{2}, \frac{1}{2})$. The CsCl unit cell in Figure 1.38 appears as BCC, but it can be described by a SC lattice and a basis that has one Cl^- ion and one Cs^+ ion. The ions in the SC unit cell are located at $(0, 0, 0)$ and at the cell center at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. Similarly, the NaCl crystal in Figure 1.37 is an FCC lattice with a basis of Na^+ and Cl^- ions.

The diamond unit cell of silicon is an FCC lattice with two Si atoms constituting the basis. The two Si atoms are placed at $(0, 0, 0)$ and $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$. Most of the important

III-V compound semiconductors such as GaAs, AlAs, InAs, InP, etc., which are widely used in numerous optoelectronic devices, have the zinc blende (ZnS) unit cell. The zinc blende unit cell consists of an FCC lattice and a basis that has the Zn and S atoms placed at $(0, 0, 0)$ and $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, respectively.

We generally represent the *geometry* of the unit cell of a lattice as a parallelepiped with sides a, b, c and angles α, β, γ as depicted in Figure 1.40a. In the case of copper and iron, the geometry of the unit cell has $a = b = c, \alpha = \beta = \gamma = 90^\circ$, and cubic

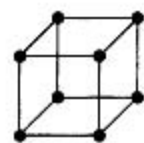
Unit Cell Geometry

Cubic system

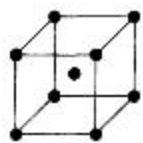
$$a = b = c$$

$$\alpha = \beta = \gamma = 90^\circ$$

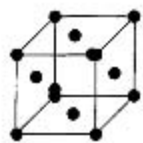
Many metals, Al, Cu, Fe, Pb. Many ceramics and semiconductors, NaCl, CsCl, LiF, Si, GaAs



Simple cubic



Body-centered cubic



Face-centered cubic

Tetragonal system

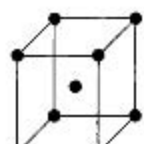
$$a = b \neq c$$

$$\alpha = \beta = \gamma = 90^\circ$$

In, Sn, barium titanate, TiO_2



Simple tetragonal



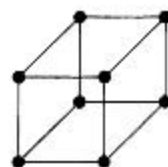
Body-centered tetragonal

Orthorhombic system

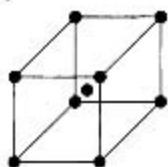
$$a \neq b \neq c$$

$$\alpha = \beta = \gamma = 90^\circ$$

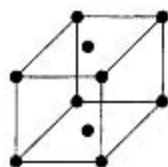
S, U, Pt, Ga ($< 30^\circ\text{C}$), iodine, cementite (Fe_3C), sodium sulfate



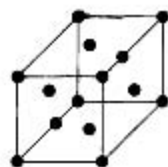
Simple orthorhombic



Body-centered orthorhombic



Base-centered orthorhombic



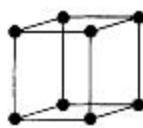
Face-centered orthorhombic

Hexagonal system

$$a = b \neq c$$

$$\alpha = \beta = 90^\circ; \gamma = 120^\circ$$

Cadmium, magnesium, zinc, graphite



Hexagonal

Rhombohedral system

$$a = b = c$$

$$\alpha = \beta = \gamma \neq 90^\circ$$

Arsenic, boron, bismuth, antimony, mercury ($< -39^\circ\text{C}$)



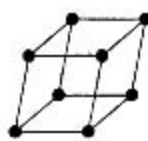
Rhombohedral

Monoclinic system

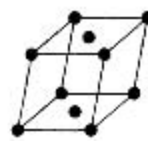
$$a \neq b \neq c$$

$$\alpha = \beta = 90^\circ; \gamma \neq 90^\circ$$

α -Selenium, phosphorus, lithium sulfate, tin fluoride



Simple monoclinic



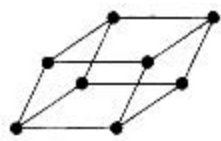
Base-centered monoclinic

Triclinic system

$$a \neq b \neq c$$

$$\alpha \neq \beta \neq \gamma \neq 90^\circ$$

Potassium dichromate



Triclinic

Figure 1.72 The seven crystal systems (unit-cell geometries) and fourteen Bravais lattices.

symmetry. For Zn, the unit cell has hexagonal geometry with $a = b \neq c$, $\alpha = \beta = 90^\circ$, and $\gamma = 120^\circ$ as shown in Figure 1.33d. Based on different lattice parameters, there are seven possible distinct unit-cell geometries, which we call **crystal systems** each with a particular distinct symmetry. The seven crystal systems are depicted in Figure 1.72 with typical examples. We are already familiar with the cubic and hexagonal systems. The seven crystal systems only categorize the unit cells based on the geometry of the unit cell and not in terms of the symmetry and periodicity of the lattice points. (One should not confuse the unit-cell geometry with the lattice, which is a periodic array of points.) In the cubic system, for example, there are three possible distinct lattices corresponding to SC, BCC, and FCC which are shown in Figure 1.72. All three have the same cubic geometry: $a = b = c$ and $\alpha = \beta = \gamma = 90^\circ$.

Many distinctly different lattices, or distinct patterns of points, exist in three dimensions. There are 14 distinct lattices whose unit cells have one of the seven geometries as indicated in Figure 1.72. Each of these is called a **Bravais lattice**. The copper crystal, for example, has the FCC Bravais lattice, but arsenic, antimony, and bismuth crystals have the rhombohedral Bravais lattice. Tin's unit cell belongs to the **tetragonal** crystal system, and its crystal lattice is a **body-centered tetragonal (BCT)**.

CD Selected Topics and Solved Problems

Selected Topics

Units and Conversions
 Bonding: Bond Energies and Elastic Moduli
 Secondary Bonding
 Cohesive Energy: Ionic Bonding and Madelung Constant
 Elementary Crystals
 X-Ray Diffraction and Crystal Structures
 Essential Mechanical Properties
 Diffusion
 Diffusion and Oxidation
 Thermal Expansion
 Surface Tension of Crystals

Solved Problems

van der Waals Bonding: Secondary Bonding and Bulk Modulus
 Elementary Concepts in Material Science: Mean Atomic Separation, Bulk and Surface Atomic Concentrations, and Density
 Elementary Crystals
 Ionic Crystals

DEFINING TERMS

Activated state is the state that occurs temporarily during a transformation or reaction when the reactant atoms or molecules come together to form a particular arrangement (intermediate between reactants and products) that has a higher potential energy than the reactants. The potential energy barrier between the activated state and the reactants is the activation energy.

Activation energy is the potential energy barrier against the formation of a product. In other words, it is the minimum energy that the reactant atom or molecule must have to be able to reach the activated state and hence form a product.

Amorphous solid is a solid that exhibits no crystalline structure or long-range order. It only possesses a

short-range order in the sense that the nearest neighbors of an atom are well defined by virtue of chemical bonding requirements.

Anion is an atom that has gained negative charge by virtue of accepting one or more electrons. Usually, atoms of nonmetallic elements can gain electrons easily to become anions. Anions become attracted to the anode (positive terminal) in ionic conduction. Typical anions are the halogen ions F^- , Cl^- , Br^- , and I^- .

Atomic mass (or relative atomic mass or atomic weight) M_{at} of an element is the average atomic mass, in atomic mass units (amu), of all the naturally occurring isotopes of the element. Atomic masses are listed in the Periodic Table. The amount of an element that has 6.022×10^{23} atoms (the Avogadro number of atoms) has a mass in grams equal to the atomic mass.

Atomic mass unit (amu) is a convenient mass measurement equal to one-twelfth of the mass of a neutral carbon atom that has a mass number of $A = 12$ (6 protons and 6 neutrons). It has been found that $amu = 1.66054 \times 10^{-27}$ kg, which is equivalent to $10^{-3}/N_A$, where N_A is Avogadro's number.

Atomic packing factor (APF) is the fraction of volume actually occupied by atoms in a crystal.

Avogadro's number (N_A) is the number of atoms in exactly 12 g of carbon-12. It is 6.022×10^{23} . Since atomic mass is defined as one-twelfth of the mass of the carbon-12 atom, the N_A number of atoms of any substance has a mass equal to the atomic mass M_{at} in grams.

Basis represents an atom, a molecule, or a collection of atoms, that is placed at each lattice point to generate the true crystal structure of a substance. All crystals are thought of as a lattice with each point occupied by a basis.

Bond energy or binding energy is the work (or energy) needed to separate two atoms infinitely from their equilibrium separation in the molecule or solid.

Bulk modulus K is volume stress (pressure) needed per unit elastic volume strain and is defined by $p = -K\Delta$, where p is the applied volume stress (pressure) and Δ is the volume strain. K indicates the extent to which a body can be reversibly (and hence elastically) deformed in volume by an applied pressure.

Cation is an atom that has gained positive charge by virtue of losing one or more electrons. Usually, metal atoms can lose electrons easily to become cations. Cations become attracted to the cathode (negative terminal) in ionic conduction, as in gaseous discharge. The alkali metals, Li, Na, K, . . . , easily lose their valence electron to become cations, Li^+ , Na^+ , K^+ , . . .

Coordination number is the number of nearest neighbors around a given atom in the crystal.

Covalent bond is the sharing of a pair of valence electrons between two atoms. For example, in H_2 , the two hydrogen atoms share their electrons, so that each has a closed shell.

Crystal is a three-dimensional periodic arrangement of atoms, molecules, or ions. A characteristic property of the crystal structure is its periodicity and a degree of symmetry. For each atom, the number of neighbors and their exact orientations are well defined; otherwise the periodicity will be lost. Therefore, a long-range order results from strict adherence to a well-defined bond length and relative bond angle (that is, exact orientation of neighbors).

Crystallization is a process by which crystals of a substance are formed from another phase of that substance. Examples are solidification just below the fusion temperature from the melt, or condensation of the molecules from the vapor phase onto a substrate. The crystallization process initially requires the formation of small crystal nuclei, which contain a limited number (perhaps 10^3 – 10^4) of atoms or molecules of the substance. Following nucleation, the nuclei grow by atomic diffusion from the melt or vapor.

Diffusion is the migration of atoms by virtue of their random thermal motions.

Diffusion coefficient is a measure of the rate at which atoms diffuse. The rate depends on the nature of the diffusion process and is typically temperature dependent. The diffusion coefficient is defined as the magnitude of diffusion flux per unit concentration gradient.

Dislocation is a line imperfection within a crystal that extends over many atomic distances.

Edge dislocation is a line imperfection within a crystal that occurs when an additional, short plane of atoms

does not extend as far as its neighbors. The edge of this short plane constitutes a line of atoms where the bonding is irregular, that is, a line of imperfection called an edge dislocation.

Elastic modulus or **Young's modulus** (Y) is a measure of the ease with which a solid can be elastically deformed. The greater Y is, the more difficult it is to deform the solid elastically. When a solid of length ℓ is subjected to a tensile stress σ (force per unit area), the solid will extend elastically by an amount $\delta\ell$ where $\delta\ell/\ell$ is the strain ϵ . Stress and strain are related by $\sigma = Y\epsilon$, so Y is the stress needed per unit elastic strain.

Electric dipole moment is formed when a positive charge $+Q$ is separated from a negative charge $-Q$ of equal magnitude. Even though the net charge is zero, there is nonetheless an electric dipole moment formed by the two charges $-Q$ and $+Q$ being separated by a finite distance. Just as two charges exert a Coulombic force on each other, two dipoles also exert an electrostatic force on each other that depends on the separation of dipoles and their relative orientation.

Electron affinity represents the energy that is needed to add an electron to a neutral atom to create a negative ion (*anion*). When an electron is added to Cl to form Cl^- , energy is actually released.

Electronegativity is a relative measure of the ability of an atom to attract the electrons in a bond it forms with another atom. The *Pauling scale of electronegativity* assigns an electronegativity value (a pure number) X to various elements, the highest being 4 for F, and the lowest values being for the alkali metal atoms, for which X are less than 1. The difference $X_A - X_B$ in the electronegativities of two atoms A and B is a measure of the polar or ionic character of the bond $A-B$ between A and B . A molecule $A-B$ would be polar, that is, possess a dipole moment, if X_A and X_B are different.

Equilibrium between two systems requires mechanical, thermal, and chemical equilibrium. Mechanical equilibrium means that the pressure should be the same in the two systems, so that one does not expand at the expense of the other. Thermal equilibrium implies that both have the same temperature. Equilibrium within a single-phase substance (*e.g.*, steam only or hydrogen

gas only) implies uniform pressure and temperature within the system.

Equilibrium state of a system is the state in which the pressure and temperature in the system are uniform throughout. We say that the system possesses mechanical and thermal equilibrium.

Eutectic composition is an alloy composition of two elements that results in the lowest melting temperature compared to any other composition. A eutectic solid has a structure that is a mixture of two phases. The eutectic structure is usually special, such as alternating lamellae.

Face-centered cubic (FCC) lattice is a cubic lattice that has one lattice point at each corner of a cube and one at the center of each face. If there is a chemical species (atom or a molecule) at each lattice point, then the structure is an FCC crystal structure.

Frenkel defect is an ionic crystal imperfection that occurs when an ion moves into an interstitial site, thereby creating a vacancy in its original site. The imperfection is therefore a pair of point defects.

Grain is an individual crystal within a polycrystalline material. Within a grain, the crystal structure and orientation are the same everywhere and the crystal is oriented in one direction only.

Grain boundary is a surface region between differently oriented, adjacent grain crystals. The grain boundary contains a lattice mismatch between adjacent grains.

Heat is the amount of energy transferred from one system to another (or between the system and its surroundings) as a result of a temperature difference. Heat is not a new form of energy, but rather the transfer of energy from one body to another by virtue of the random motions of their molecules. When a hot body is in contact with a cold body, energy is transferred from the hot body to the cold one. The energy that is transferred is the excess mean kinetic energy of the molecules in the hot body. Molecules in the hot body have a higher mean kinetic energy and vibrate more violently. As a result of the collisions between the molecules, there is a net transfer of energy (heat) from the hot body to the cold one, until the molecules in both bodies have the same mean kinetic energy, that is, until their temperatures become equal.

Heat capacity at constant volume is the increase in the total energy E of the system per degree increase in the

temperature of the system with the volume remaining constant: $C = (\partial E / \partial T)_V$. Thus, the heat added to the system does no mechanical work due to a volume change but increases the internal energy. **Molar heat capacity** is the heat capacity for 1 mole of a substance. **Specific heat capacity** is the heat capacity per unit mass.

Interstitial site (interstice) is an unoccupied space between the atoms (or ions, or molecules) in a crystal.

Ionization energy is the energy required to remove an electron from a neutral atom; normally the most outer electron that has the least binding energy to the nucleus is removed to ionize an atom.

Isomorphous describes a structure that is the same everywhere (from *iso*, uniform, and *morphology*, structure).

Isotropic substance is a material that has the same property in all directions.

Kinetic molecular theory assumes that the atoms and molecules of all substances (gases, liquids, and solids) above absolute zero of temperature are in constant motion. Monatomic molecules (e.g., He, Ne) in a gas exhibit constant and random translational motion, whereas the atoms in a solid exhibit constant vibrational motion.

Lattice is a regular array of points in space with a discernible periodicity. There are 14 distinct lattices possible in three-dimensional space. When an atom or molecule is placed at each lattice point, the resulting regular structure is a crystal structure.

Lattice parameters are (a) the lengths of the sides of the unit cell, and (b) the angles between the sides.

Mechanical work is qualitatively defined as the energy expended in displacing a constant force through a distance. When a force \mathbf{F} is moved a distance $d\mathbf{x}$, work done $dW = \mathbf{F} \cdot d\mathbf{x}$. When we lift a body such as an apple of mass m (100 g) by a distance h (1 m), we do work by an amount $F \Delta x = mgh$ (1 J), which is then stored as the gravitational potential energy of the body. We have transferred energy from ourselves to the potential energy of the body by exchanging energy with it in the form of work. Further, in lifting the apple, the molecules have been displaced in orderly fashion, all upwards. Work therefore involves an orderly displacement of atoms and molecules of a substance in

complete contrast to heat. When the volume V of a substance changes by dV when the pressure is P , the mechanical work involved is $P dV$ and is called the **PV work**.

Metallic bonding is the binding of metal atoms in a crystal through the attraction between the positive metal ions and the mobile valence electrons in the crystal. The valence electrons permeate the space between the ions.

Miller indices (hkl) are indices that conveniently identify parallel planes in a crystal. Consider a plane with the intercepts, x_1 , y_1 , and z_1 , in terms of lattice parameters a , b , and c . (For a plane passing through the origin, we shift the origin or use a parallel plane.) Then, (hkl) are obtained by taking the reciprocals of x_1 , y_1 , and z_1 and clearing all fractions.

Miscibility of two substances is a measure of the mutual solubility of those two substances when they are in the same phase, such as liquid.

Mole of a substance is that amount of the substance that contains N_A number of atoms (or molecules), where N_A is Avogadro's number (6.023×10^{23}). One mole of a substance has a mass equal to its atomic (molecular) mass, in grams. For example, 1 mole of copper contains 6.023×10^{23} atoms and has a mass of 63.55 g.

Phase of a system is a homogeneous portion of the chemical system that has the same composition, structure, and properties everywhere. In a given chemical system, one phase may be in contact with another phase of the system. For example, iced water at 0°C will have solid and liquid phases in contact. Each phase, solid ice and liquid water, has a distinct structure.

Phase diagram is a temperature versus composition diagram in which the existence and coexistence of various phases are identified by regions and lines. Between the liquidus and solidus lines, for example, the material is a heterogeneous mixture of the liquid and solid phases.

Planar concentration of atoms is the number of atoms per unit area on a given (hkl) plane in a crystal.

Polarization is the separation of positive and negative charges in a system, which results in a net electric dipole moment.

Polymorphism or **allotropy** is a material attribute that allows the material to possess more than one crystal structure. Each possible crystal structure is called a polymorph. Generally, the structure of the polymorph depends on the temperature and pressure, as well as on the method of preparation of the solid. (For example, diamond can be prepared from graphite by the application of very high pressures.)

Primary bond is a strong interatomic bond, typically greater than 1 eV/atom, that involves ionic, covalent, or metallic bonding.

Property is a system characteristic or an attribute that we can measure. Pressure, volume, temperature, mass, energy, electrical resistivity, magnetization, polarization, and color are all properties of matter. Properties such as pressure, volume, and temperature can only be attributed to a system of many particles (which we treat as a continuum). Note that heat and work are not properties of a substance; instead, they represent energy transfers involved in producing changes in the properties.

Saturated solution is a solution that has the maximum possible amount of solute dissolved in a given amount of solvent at a specified temperature and pressure.

Schottky defect is an ionic crystal imperfection that occurs when a pair of ions is missing, that is, when there is a cation and anion pair vacancy.

Screw dislocation is a crystal defect that occurs when one portion of a perfect crystal is twisted or skewed with respect to another portion on only one side of a line.

Secondary bond is a weak bond, typically less than 0.1 eV/atom, which is due to dipole-dipole interactions between the atoms or molecules.

Solid solution is a homogeneous crystalline phase that contains two or more chemical components.

Solute is the minor chemical component of a solution; the component that is usually added in small amounts to a solvent to form a solution.

Solvent is the major chemical component of a solution.

Stoichiometric compounds are compounds with an integer ratio of atoms, as in CaF_2 , in which two fluorine atoms bond with one calcium atom.

Strain is a relative measure of the deformation a material exhibits under an applied stress. Under an applied tensile (or compressive) stress, strain ϵ is the change in the length per unit original length. When a shear stress is applied, the deformation involves a shear angle. **Shear strain** is the tangent of the shear angle that is developed by the application of the shearing stress. **Volume strain** Δ is the change in the volume per unit original volume.

Stress is force per unit area. When the applied force F is perpendicular to the area A , stress $\sigma = F/A$ is either tensile or compressive. If the applied force is tangential to the area, then stress is **shear stress**, $\tau = F/A$.

Thermal expansion is the change in the length or volume of a substance due to a change in the temperature.

Linear coefficient of thermal expansion λ is the fractional change in the length per unit temperature change or $\Delta L/L_0 = \lambda \Delta T$. **Volume coefficient of expansion** α_v is the fractional change in the volume per unit temperature change; $\alpha_v \approx 3\lambda$.

Unit cell is the most convenient small cell in a crystal structure that carries the characteristics of the crystal. The repetition of the unit cell in three dimensions generates the whole crystal structure.

Vacancy is a point defect in a crystal, where a normally occupied lattice site is missing an atom.

Valence electrons are the electrons in the outer shell of an atom. Since they are the farthest away from the nucleus, they are the first electrons involved in atom-to-atom interactions.

Young's modulus see **elastic modulus**.

QUESTIONS AND PROBLEMS

- 1.1 **Virial theorem** The Li atom has a nucleus with a $+3e$ positive charge, which is surrounded by a full $1s$ shell with two electrons, and a single valence electron in the outer $2s$ subshell. The atomic radius of the Li atom is about 0.17 nm. Using the Virial theorem, and assuming that the valence electron sees the nuclear $+3e$ shielded by the two $1s$ electrons, that is, a net charge of $+e$, estimate the ionization energy

of Li (the energy required to free the $2s$ electron). Compare this value with the experimental value of 5.39 eV. Suppose that the actual nuclear charge seen by the valence electron is not $+e$ but a little higher, say $+1.25e$, due to the imperfect shielding provided by the closed $1s$ shell. What would be the new ionization energy? What is your conclusion?

1.2 Atomic mass and molar fractions

- a. Consider a multicomponent alloy containing N elements. If w_1, w_2, \dots, w_N are the weight fractions of components 1, 2, \dots , N in the alloy and M_1, M_2, \dots, M_N are the respective atomic masses of the elements, show that the atomic fraction of the i th component is given by

$$n_i = \frac{w_i / M_i}{\frac{w_1}{M_1} + \frac{w_2}{M_2} + \dots + \frac{w_N}{M_N}} \quad \text{Weight to atomic percentage}$$

- b. Suppose that a substance (compound or an alloy) is composed of N elements, A, B, C, \dots and that we know their atomic (or molar) fractions n_A, n_B, n_C, \dots . Show that the weight fractions w_A, w_B, w_C, \dots are given by

$$w_A = \frac{n_A M_A}{n_A M_A + n_B M_B + n_C M_C + \dots} \quad \text{Atomic to weight percentage}$$

$$w_B = \frac{n_B M_B}{n_A M_A + n_B M_B + n_C M_C + \dots}$$

- c. Consider the semiconducting II-VI compound cadmium selenide, CdSe. Given the atomic masses of Cd and Se, find the weight fractions of Cd and Se in the compound and grams of Cd and Se needed to make 100 grams of CdSe.
- d. A Se-Te-P glass alloy has the composition 77 wt.% Se, 20 wt.% Te, and 3 wt.% P. Given their atomic masses, what are the atomic fractions of these constituents?

- ### 1.3 The covalent bond
- Consider the H_2 molecule in a simple way as two touching H atoms, as depicted in Figure 1.73. Does this arrangement have a lower energy than two separated H atoms? Suppose that electrons totally correlate their motions so that they move to avoid each other as in the snapshot in Figure 1.73. The radius r_0 of the hydrogen atom is 0.0529 nm. The electrostatic potential energy of two charges Q_1 and Q_2 separated by a distance r is given by $Q_1 Q_2 / (4\pi\epsilon_0 r)$. Using the virial theorem as in Example 1.1 consider the following:

- a. Calculate the total electrostatic potential energy PE of all the charges when they are arranged as shown in Figure 1.73. In evaluating the PE of the whole collection of charges you must consider all pairs of charges and, at the same time, avoid double counting of interactions between the same pair of charges. The total PE is the sum of the following: electron 1 interacting with the proton at a distance r_0 on the left, proton at r_0 on the right, and electron 2 at a distance $2r_0 +$ electron 2 interacting with a proton at r_0 and another proton at $3r_0 +$ two protons, separated by $2r_0$, interacting with each other. Is this configuration energetically favorable?
- b. Given that in the isolated H atom the PE is $2 \times (-13.6 \text{ eV})$, calculate the change in PE in going from two isolated H atoms to the H_2 molecule. Using the virial theorem, find the change in the total energy and hence the covalent bond energy. How does this compare with the experimental value of 4.51 eV?

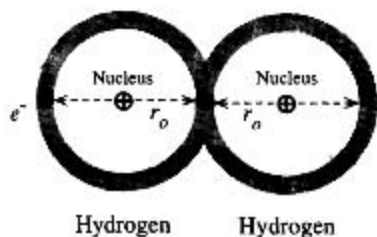


Figure 1.73 A simplified view of the covalent bond in H_2 . A snapshot at one instant.

- 1.4 **Ionic bonding and CsCl** The potential energy E per Cs^+-Cl^- pair within the CsCl crystal depends on the interionic separation r in the same fashion as in the NaCl crystal,

$$E(r) = -\frac{e^2 M}{4\pi\epsilon_0 r} + \frac{B}{r^m} \quad [1.38]$$

where for CsCl, $M = 1.763$, $B = 1.192 \times 10^{-104} \text{ J m}^9$ or $7.442 \times 10^{-5} \text{ eV (nm)}^9$, and $m = 9$. Find the equilibrium separation (r_0) of the ions in the crystal and the ionic bonding energy, that is, the ionic cohesive energy, and compare the latter value to the experimental value of 657 kJ mol^{-1} . Given that the *ionization energy* of Cs is 3.89 eV and the *electron affinity* of Cl (energy released when an electron is added) is 3.61 eV , calculate the atomic cohesive energy of the CsCl crystal as joules per mole.

- 1.5 **Madelung constant** If we were to examine the NaCl crystal in three dimensions, we would find that each Na^+ ion has

- 6 Cl^- ions as *nearest* neighbors at a distance r
 12 Na^+ ions as *second* nearest neighbors at a distance $r\sqrt{2}$
 8 Cl^- ions as *third* nearest neighbors at a distance $r\sqrt{3}$

and so on. Show that the electrostatic potential energy of the Na^+ atom can be written as

$$E(r) = -\frac{e^2}{4\pi\epsilon_0 r} \left[6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \dots \right] = -\frac{e^2 M}{4\pi\epsilon_0 r}$$

where M , called the **Madelung constant**, is given by the summation in the square brackets for this particular ionic crystal structure (NaCl). Calculate M for the first three terms and compare it with $M = 1.7476$, its value had we included the higher terms. What is your conclusion?

- *1.6 **Bonding and bulk modulus** In general, the potential energy E per atom, or per ion pair, in a crystal as a function of interatomic (interionic) separation r can be written as the sum of an attractive PE and a repulsive PE ,

$$E(r) = -\frac{A}{r^n} + \frac{B}{r^m} \quad [1.39]$$

where A and n are constants characterizing the attractive PE and B and m are constants characterizing the repulsive PE . This energy is minimum when the crystal is in equilibrium. The magnitude of the minimum energy and its location r_0 define the bonding energy and the equilibrium interatomic (or interionic) separation, respectively.

When a pressure P is applied to a solid, its original volume V_0 shrinks to V by an amount $\Delta V = V - V_0$. The bulk modulus K relates the volume strain $\Delta V/V$ to the applied pressure P by

$$P = -K \frac{\Delta V}{V_0} \quad [1.40]$$

The bulk modulus K is related to the energy curve. In its simplest form (assuming a simple cubic unit cell) K can be estimated from Equation 1.39 by

$$K = \frac{1}{9cr_0} \left[\frac{d^2 E}{dr^2} \right]_{r=r_0} \quad [1.41]$$

where c is a numerical factor, of the order of unity, given by b/p where p is the number of atoms or ion pairs in the unit cell and b is a numerical factor that relates the cubic unit cell lattice parameter a_0 to the equilibrium interatomic (interionic) separation r_0 by $b = a_0^3/r_0^3$.

- a. Show that the bond energy and equilibrium separation are given by

$$E_{\text{bond}} = \frac{A}{r_0^n} \left(1 - \frac{n}{m} \right) \quad \text{and} \quad r_0 = \left(\frac{Bm}{An} \right)^{1/(m-n)}$$

Energy per ion pair in ionic crystals

Madelung constant M for NaCl

General PE curve for bonding

Bulk modulus definition

Bulk modulus

- b. Show that the bulk modulus is given by

$$K = \frac{An}{9cr_0^{n+3}}(m-n) \quad \text{or} \quad K = \frac{mnE_{\text{bond}}}{9cr_0^3}$$

- c. For a NaCl-type crystal, Na^+ and Cl^- ions touch along the cube edge so that $r_0 = (a_0/2)$. Thus, $a^3 = 2^3r_0^3$ and $b = 2^3 = 8$. There are four ion pairs in the unit cell, $p = 4$. Thus, $c = b/p = 8/4 = 2$. Using the values from Example 1.2, calculate the bulk modulus of NaCl.

- *1.7 **Van der Waals bonding** Below 24.5 K, Ne is a crystalline solid with an FCC structure. The interatomic interaction energy per atom can be written as

$$E(r) = -2\varepsilon \left[14.45 \left(\frac{\sigma}{r} \right)^6 - 12.13 \left(\frac{\sigma}{r} \right)^{12} \right] \quad (\text{eV/atom})$$

where ε and σ are constants that depend on the polarizability, the mean dipole moment, and the extent of overlap of core electrons. For crystalline Ne, $\varepsilon = 3.121 \times 10^{-3}$ eV and $\sigma = 0.274$ nm.

- a. Show that the equilibrium separation between the atoms in an inert gas crystal is given by $r_0 = (1.090)\sigma$. What is the equilibrium interatomic separation in the Ne crystal?
 b. Find the bonding energy per atom in solid Ne.
 c. Calculate the density of solid Ne (atomic mass = 20.18).

1.8 Kinetic molecular theory

- a. In a particular Ar-ion laser tube the gas pressure due to Ar atoms is about 0.1 torr at 25 °C when the laser is off. What is the concentration of Ar atoms per cm^3 at 25 °C in this laser? (760 torr = 1 atm = 1.013×10^5 Pa.)
 b. In the He–Ne laser tube He and Ne gases are mixed and sealed. The total pressure P in the gas is given by contributions arising from He and Ne atoms:

$$P = P_{\text{He}} + P_{\text{Ne}}$$

where P_{He} and P_{Ne} are the *partial pressures* of He and Ne in the gas mixture, that is, pressures due to He and Ne gases alone,

$$P_{\text{He}} = \frac{N_{\text{He}}}{N_A} \left(\frac{RT}{V} \right) \quad \text{and} \quad P_{\text{Ne}} = \frac{N_{\text{Ne}}}{N_A} \left(\frac{RT}{V} \right)$$

In a particular He–Ne laser tube the ratio of He and Ne atoms is 7:1, and the total pressure is about 1 torr at 22 °C. Calculate the concentrations of He and Ne atoms in the gas at 22 °C. What is the pressure at an operating temperature of 130 °C?

- 1.9 **Kinetic molecular theory** Calculate the effective (rms) speeds of the He and Ne atoms in the He–Ne gas laser tube at room temperature (300 K).

- *1.10 **Kinetic molecular theory and the Ar-ion laser** An argon-ion laser has a laser tube that contains Ar atoms that produce the laser emission when properly excited by an electrical discharge. Suppose that the gas temperature inside the tube is 1300 °C (very hot).

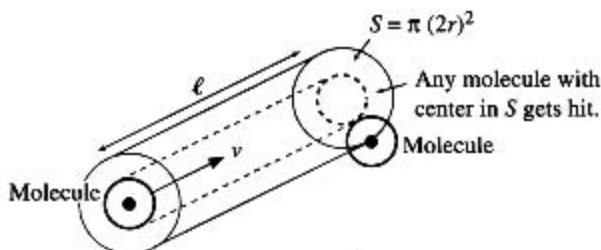
- a. Calculate the mean speed (v_{av}), rms velocity ($v_{\text{rms}} = \sqrt{v^2}$), and the rms speed ($v_{\text{rms},x} = \sqrt{v_x^2}$) in one particular direction of the Ar atoms in the laser tube, assuming 1300 °C. (See Example 1.10.)
 b. Consider a light source that is emitting waves and is moving toward an observer, somewhat like a whistling train moving toward a passenger. If f_0 is the frequency of the light waves emitted at the source, then, due to the *Doppler effect*, the observer measures a higher frequency f that depends on the velocity v_{Ar} of the source moving toward the observer and the speed c of light,

$$f = f_0 \left(1 + \frac{v_{\text{Ar}}}{c} \right)$$

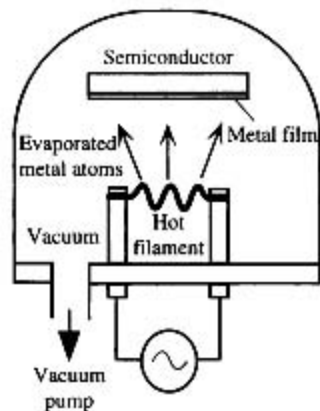
It is the Ar ions that emit the laser output light in the Ar-ion laser. The emission wavelength $\lambda_0 = c/f_0$ is 514.5 nm. Calculate the wavelength λ registered by an observer for those atoms that are moving with a mean speed v_{av} toward the observer. Those atoms that are moving away from the observer will result in a lower observed frequency because v_{Ar} will be negative. Estimate the width of the wavelengths (the difference between the longest and shortest wavelengths) emitted by the Ar-ion laser.

***1.11 Vacuum deposition** Consider air as composed of nitrogen molecules N_2 .

- What is the concentration n (number of molecules per unit volume) of N_2 molecules at 1 atm and 27 °C?
- Estimate the mean separation between the N_2 molecules.
- Assume each molecule has a finite size that can be represented by a sphere of radius r . Also assume that ℓ is the **mean free path**, defined as the mean distance a molecule travels before colliding with another molecule, as illustrated in Figure 1.74a. If we consider the motion of one N_2 molecule, with all the others stationary, it is apparent that if the path of the traveling molecule crosses the cross-sectional area $S = \pi(2r)^2$, there will be a collision. Since ℓ is the mean distance between collisions, there must be at least one stationary molecule within the volume $S\ell$,



(a) A molecule moving with a velocity v travels a mean distance ℓ between collisions. Since the collision cross-sectional area is S , in the volume $S\ell$ there must be at least one molecule. Consequently, $n(S\ell) = 1$.



(b) Vacuum deposition of metal electrodes by thermal evaporation.

Figure 1.74

Walter Houser Brattain (1902–1987), experimenting with metal contacts on copper oxide (1935) at Bell Telephone Labs. A vacuum evaporation chamber is used to deposit the metal electrode.

| SOURCE: Bell Telephone Laboratories, courtesy AIP Emilio Segrè Visual Archives.

as shown in Figure 1.74a. Since n is the concentration, we must have $n(S\ell) = 1$ or $\ell = 1/(\pi 4r^2 n)$. However, this must be corrected for the fact that all the molecules are in motion, which only introduces a numerical factor, so that

$$\ell = \frac{1}{2^{1/2} 4\pi r^2 n}$$

Assuming a radius r of 0.1 nm, calculate the mean free path of N_2 molecules between collisions at 27 °C and 1 atm.

- d. Assume that an Au film is to be deposited onto the surface of a Si chip to form metallic interconnections between various devices. The deposition process is generally carried out in a vacuum chamber and involves the condensation of Au atoms from the vapor phase onto the chip surface. In one procedure, a gold wire is wrapped around a tungsten filament, which is heated by passing a large current through the filament (analogous to the heating of the filament in a light bulb) as depicted in Figure 1.74b. The Au wire melts and wets the filament, but as the temperature of the filament increases, the gold evaporates to form a vapor. Au atoms from this vapor then condense onto the chip surface, to solidify and form the metallic connections. Suppose that the source (filament)-to-substrate (chip) distance L is 10 cm. Unless the mean free path of air molecules is much longer than L , collisions between the metal atoms and air molecules will prevent the deposition of the Au onto the chip surface. Taking the mean free path ℓ to be $100L$, what should be the pressure inside the vacuum system? (Assume the same r for Au atoms.)

1.12 Heat capacity

- a. Calculate the heat capacity per mole and per gram of N_2 gas, neglecting the vibrations of the molecule. How does this compare with the experimental value of $0.743 \text{ J g}^{-1} \text{ K}^{-1}$?
- b. Calculate the heat capacity per mole and per gram of CO_2 gas, neglecting the vibrations of the molecule. How does this compare with the experimental value of $0.648 \text{ J K}^{-1} \text{ g}^{-1}$? Assume that the CO_2 molecule is linear (O-C-O) so that it has two rotational degrees of freedom.
- c. Based on the Dulong-Petit rule, calculate the heat capacity per mole and per gram of solid silver. How does this compare with the experimental value of $0.235 \text{ J K}^{-1} \text{ g}^{-1}$?
- d. Based on the Dulong-Petit rule, calculate the heat capacity per mole and per gram of the silicon crystal. How does this compare with the experimental value of $0.71 \text{ J K}^{-1} \text{ g}^{-1}$?

- 1.13 **Dulong-Petit atomic heat capacity** Express the Dulong-Petit rule for the molar heat capacity as heat capacity per atom and in the units of eV K^{-1} per atom, called the **atomic heat capacity**. CsI is an ionic crystal used in optical applications that require excellent infrared transmission at very long wavelengths (up to 55 μm). It has the CsCl crystal structure with one Cs^+ and one I^- ion in the unit cell. Given the density of CsI as 4.51 g cm^{-3} , calculate the specific heat capacity of CsI and compare it with the experimental value of $0.2 \text{ J K}^{-1} \text{ g}^{-1}$. What is your conclusion?

1.14 Dulong-Petit specific heat capacity of alloys and compounds

- a. Consider an alloy AB , such as solder, or a compound material such as MgO , composed of n_A , atomic fractions of A , and n_B , atomic fractions of B . (The atomic fraction of A is the same as its molar fraction.) Let M_A and M_B be the atomic weights of A and B , in g mol^{-1} . The mean atomic weight per atom in the alloy or compound is then

$$\bar{M} = n_A M_A + n_B M_B$$

Average atomic weight

Show that the *Dulong-Petit rule* for the specific heat capacity c_s leads to

$$c_s = \frac{C_m}{\bar{M}} = \frac{25}{n_A M_A + n_B M_B} \text{ J K}^{-1} \text{ g}^{-1}$$

Specific heat capacity

- b. Calculate the specific heat capacity of Pb-Sn solder assuming that its composition is 38 wt.% Pb and 62 wt.% Sn.

- c. Calculate the specific heat capacities of Pb and Sn individually as c_{FA} and c_{FB} , respectively, and then calculate the c_F for the alloy using

$$c_F = c_{FA}w_A + c_{FB}w_B$$

where w_A and w_B are the weight fractions of A (Pb) and B (Sn) in the alloy (solder). Compare your result with part (a). What is your conclusion?

- d. ZnSe is an important optical material (used in infrared windows and lenses and high-power CO₂ laser optics) and also an important II–VI semiconductor that can be used to fabricate blue-green laser diodes. Calculate the specific heat capacity of ZnSe, and compare the calculation to the experimental value of $0.345 \text{ J K}^{-1} \text{ g}^{-1}$.

Alloy specific heat capacity

1.15 Thermal expansion

- a. If λ is the thermal expansion coefficient, show that the thermal expansion coefficient for an area is 2λ . Consider an aluminum square sheet of area 1 cm^2 . If the thermal expansion coefficient of Al at room temperature (25°C) is about $24 \times 10^{-6} \text{ K}^{-1}$, at what temperature is the percentage change in the area +1%?
- b. A particular incandescent light bulb (100 W, 120 V) has a tungsten (W) filament of length 57.9 cm and a diameter of $63.5 \mu\text{m}$. Calculate the length of the filament at 2300°C , the approximate operating temperature of the filament inside the bulb. The linear expansion coefficient λ of W is approximately $4.50 \times 10^{-6} \text{ K}^{-1}$ at 300 K. How would you improve your calculation?

1.16 Thermal expansion of Si

The expansion coefficient of silicon over the temperature range 120–1500 K is given by Okada and Tokumaru (1984) as

$$\lambda = 3.725 \times 10^{-6} [1 - e^{-3.725 \times 10^{-3}(T-124)}] + 5.548 \times 10^{-10} T$$

where λ is in K^{-1} (or $^\circ\text{C}^{-1}$) and T is in kelvins.

- a. By expanding the above function around 20°C (293 K) show that,

$$\lambda = 2.5086 \times 10^{-6} + (8.663 \times 10^{-9})(T - 293) - (2.3839 \times 10^{-11})(T - 293)^2$$

- b. The change $\delta\rho$ in the density due to a change δT in the temperature, from Example 1.5, is given by

$$\delta\rho = -\rho_0\alpha_V \delta T = -3\rho_0\lambda \delta T$$

Given the density of Si as 2.329 g cm^{-3} at 20°C , calculate the density at 1000°C by using the full expression and by using the polynomials expansion of λ . What is your conclusion?

Silicon linear expansion coefficient

Silicon linear expansion coefficient

1.17 Thermal expansion of GaP and GaAs

- a. GaP has the zinc blende structure. The linear expansion coefficient in GaP has been measured as follows: $\lambda = 4.65 \times 10^{-6} \text{ K}^{-1}$ at 300 K; $5.27 \times 10^{-6} \text{ K}^{-1}$ at 500 K; $5.97 \times 10^{-6} \text{ K}^{-1}$ at 800 K. Calculate the coefficients, A, B, and C in

$$\frac{dL}{L_0 dT} = \lambda(T) = A + B(T - T_0) + C(T - T_0)^2 + \dots$$

where $T_0 = 300 \text{ K}$. The lattice constant of GaP, a , at 27°C is 0.5451 nm . Calculate the lattice constant at 300°C .

- b. The linear expansion coefficient of GaAs over 200–1000 K is given by

$$\lambda = 4.25 \times 10^{-6} + (5.82 \times 10^{-9})T - (2.82 \times 10^{-12})T^2$$

where T is in kelvins. The lattice constant a at 300 K is 0.56533 nm . Calculate the lattice constant and the density at -40°C .

GaAs linear expansion coefficient

1.18 Electrical noise

Consider an amplifier with a bandwidth B of 5 kHz, corresponding to a typical speech bandwidth. Assume the input resistance of the amplifier is $1 \text{ M}\Omega$. What is the rms noise voltage at the input? What will happen if the bandwidth is doubled to 10 kHz? What is your conclusion?

- 1.19 Thermal activation** A certain chemical oxidation process (e.g., SiO_2) has an activation energy of 2 eV atom^{-1} .
- Consider the material exposed to pure oxygen gas at a pressure of 1 atm at 27°C . Estimate how many oxygen molecules per unit volume will have energies in excess of 2 eV ? (Consider the numerical integration of Equation 1.24.)
 - If the temperature is 900°C , estimate the number of oxygen molecules with energies more than 2 eV . What happens to this concentration if the pressure is doubled?
- 1.20 Diffusion in Si** The diffusion coefficient of boron (B) atoms in a single crystal of Si has been measured to be $1.5 \times 10^{-18} \text{ m}^2 \text{ s}^{-1}$ at 1000°C and $1.1 \times 10^{-16} \text{ m}^2 \text{ s}^{-1}$ at 1200°C .
- What is the activation energy for the diffusion of B, in eV/atom ?
 - What is the preexponential constant D_0 ?
 - What is the rms distance (in micrometers) diffused in 1 hour by the B atom in the Si crystal at 1200°C and 1000°C ?
 - The diffusion coefficient of B in polycrystalline Si has an activation energy of $2.4\text{--}2.5 \text{ eV/atom}$ and $D_0 = (1.5\text{--}6) \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$. What constitutes the diffusion difference between the single crystal sample and the polycrystalline sample?
- 1.21 Diffusion in SiO_2** The diffusion coefficient of P atoms in SiO_2 has an activation energy of 2.30 eV/atom and $D_0 = 5.73 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. What is the rms distance diffused in 1 hour by P atoms in SiO_2 at 1200°C ?
- 1.22 BCC and FCC crystals**
- Molybdenum has the BCC crystal structure, a density of 10.22 g cm^{-3} , and an atomic mass of 95.94 g mol^{-1} . What is the atomic concentration, lattice parameter a , and atomic radius of molybdenum?
 - Gold has the FCC crystal structure, a density of 19.3 g cm^{-3} , and an atomic mass of $196.97 \text{ g mol}^{-1}$. What is the atomic concentration, lattice parameter a , and atomic radius of gold?
- 1.23 BCC and FCC crystals**
- Tungsten (W) has the BCC crystal structure. The radius of the W atom is 0.1371 nm . The atomic mass of W is 183.8 amu (g mol^{-1}). Calculate the number of W atoms per unit volume and density of W.
 - Platinum (Pt) has the FCC crystal structure. The radius of the Pt atom is 0.1386 nm . The atomic mass of Pt is 195.09 amu (g mol^{-1}). Calculate the number of Pt atoms per unit volume and density of Pt.
- 1.24 Planar and surface concentrations** Niobium (Nb) has the BCC crystal with a lattice parameter $a = 0.3294 \text{ nm}$. Find the planar concentrations as the number of atoms per nm^2 of the (100), (110), and (111) planes. Which plane has the most concentration of atoms per unit area? Sometimes the number of atoms per unit area n_{surface} on the surface of a crystal is estimated by using the relation $n_{\text{surface}} = n_{\text{bulk}}^{2/3}$, where n_{bulk} is the concentration of atoms in the bulk. Compare n_{surface} values with the planar concentrations that you calculated and comment on the difference. [Note: The BCC (111) plane does not cut through the center atom and the (111) has one-sixth of an atom at each corner.]
- 1.25 Diamond and zinc blende** Si has the diamond and GaAs has the zinc blende crystal structure. Given the lattice parameters of Si and GaAs, $a = 0.357 \text{ nm}$ and $a = 0.356 \text{ nm}$, respectively, and the atomic masses of Si, Ga, and As as 28.08 , 69.73 , and 74.92 , respectively, calculate the density of Si and GaAs. What is the atomic concentration (atoms per unit volume) in each crystal?
- 1.26 Zinc blende, NaCl, and CsCl**
- InAs is a III-V semiconductor that has the zinc blende structure with a lattice parameter of 0.606 nm . Given the atomic masses of In ($114.82 \text{ g mol}^{-1}$) and As (74.92 g mol^{-1}), find the density.
 - CdO has the NaCl crystal structure with a lattice parameter of 0.4695 nm . Given the atomic masses of Cd ($112.41 \text{ g mol}^{-1}$) and O (16.00 g mol^{-1}), find the density.

- c. KCl has the same crystal structure as NaCl. The lattice parameter a of KCl is 0.629 nm. The atomic masses of K and Cl are 39.10 g mol^{-1} and 35.45 g mol^{-1} , respectively. Calculate the density of KCl.

1.27 Crystallographic directions and planes Consider the cubic crystal system.

- a. Show that the line $[hkl]$ is perpendicular to the (hkl) plane.
 b. Show that the spacing between adjacent (hkl) planes is given by

$$d = \frac{a}{\sqrt{h^2 + k^2 + \ell^2}}$$

1.28 Si and SiO₂

- a. Given the Si lattice parameter $a = 0.543 \text{ nm}$, calculate the number of Si atoms per unit volume, in nm^{-3} .
 b. Calculate the number of atoms per m^2 and per nm^2 on the (100), (110), and (111) planes in the Si crystal as shown in Figure 1.75. Which plane has the most number of atoms per unit area?
 c. The density of SiO₂ is 2.27 g cm^{-3} . Given that its structure is amorphous, calculate the number of molecules per unit volume, in nm^{-3} . Compare your result with (a) and comment on what happens when the surface of an Si crystal oxidizes. The atomic masses of Si and O are 28.09 and 16, respectively.

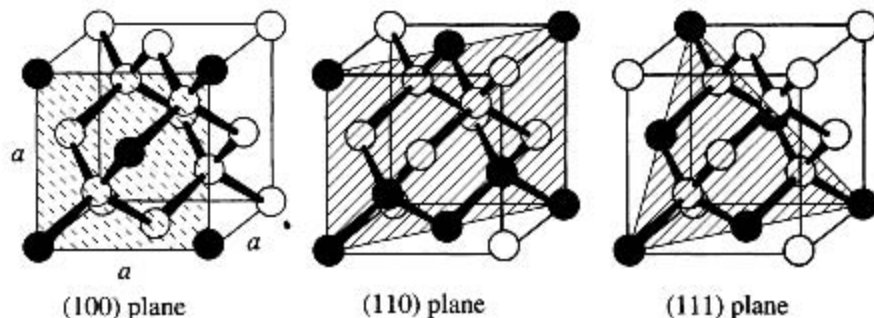


Figure 1.75 Diamond cubic crystal structure and planes.

Determine what portion of a black-colored atom belongs to the plane that is hatched.

1.29 Vacancies in metals

- a. The energy of formation of a vacancy in the copper crystal is about 1 eV. Calculate the concentration of vacancies at room temperature (300 K) and just below the melting temperature, 1084°C . Neglect the change in the density which is small.
 b. The following table shows the energies of vacancy formation in various metals with *close-packed* crystal structures and the melting temperature T_m . Plot E_v in eV versus T_m in kelvins, and explore if there is a correlation between a and T_m . Some materials engineers take E_v to be very roughly $10kT_m$. Do you think that they are correct? (Justify.)

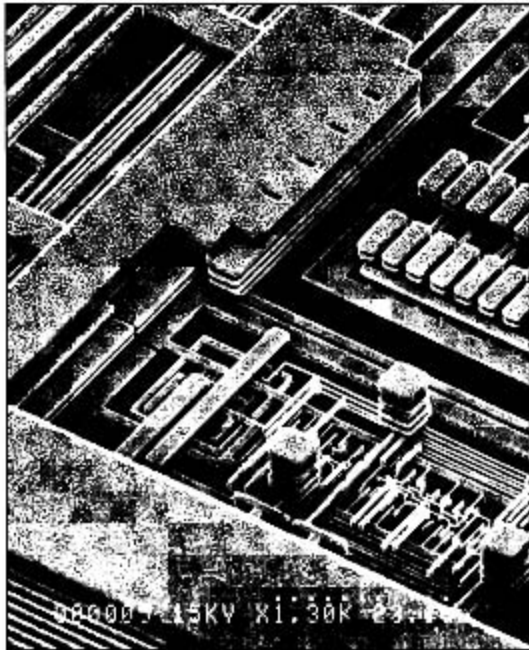
	Metal								
	Al	Ag	Au	Cu	Mg	Pt	Pb	Ni	Pd
Crystal	FCC	FCC	FCC	FCC	HCP	FCC	FCC	FCC	FCC
E_v (eV)	0.70–0.76	1.0–1.1	0.90–0.98	1–1.28	0.89	1.3–1.5	0.50	1.63–1.79	1.54–1.85
T_m ($^\circ\text{C}$)	660	962	1064	1085	650	1768	328	1455	1555

- 1.30 Vacancies in silicon** In device fabrication, Si is frequently doped by the diffusion of impurities (dopants) at high temperatures, typically 950–1200°C. The energy of vacancy formation in the Si crystal is about 3.6 eV. What is the equilibrium concentration of vacancies in a Si crystal at 1000 °C? Neglect the change in the density with temperature which is less than 1 percent in this case.
- 1.31 Pb–Sn solder** Consider the soldering of two copper components. When the solder melts, it wets both metal surfaces. If the surfaces are not clean or have an oxide layer, the molten solder cannot wet the surfaces and the soldering fails. Assume that soldering takes place at 250 °C, and consider the diffusion of Sn atoms into the copper (the Sn atom is smaller than the Pb atom and hence diffuses more easily).
- The diffusion coefficient of Sn in Cu at two temperatures is $D = 1.69 \times 10^{-9} \text{ cm}^2 \text{ hr}^{-1}$ at 400 °C and $D = 2.48 \times 10^{-7} \text{ cm}^2 \text{ hr}^{-1}$ at 650 °C. Calculate the rms distance diffused by an Sn atom into the copper, assuming the cooling process takes 10 seconds.
 - What should be the composition of the solder if it is to begin freezing at 250 °C?
 - What are the components (phases) in this alloy at 200 °C? What are the compositions of the phases and their relative weights in the alloy?
 - What is the microstructure of this alloy at 25 °C? What are weight fractions of the α and β phases assuming near equilibrium cooling?
- 1.32 Pb–Sn solder** Consider 50% Pb–50% Sn solder.
- Sketch the temperature-time profile and the microstructure of the alloy at various stages as it is cooled from the melt.
 - At what temperature does the solid melt?
 - What is the temperature range over which the alloy is a mixture of melt and solid? What is the structure of the solid?
 - Consider the solder at room temperature following cooling from 182 °C. Assume that the rate of cooling from 182 °C to room temperature is faster than the atomic diffusion rates needed to change the compositions of the α and β phases in the solid. Assuming the alloy is 1 kg, calculate the masses of the following components in the solid:
 - The primary α .
 - α in the whole alloy.
 - α in the eutectic solid.
 - β in the alloy. (Where is the β -phase?)
 - Calculate the specific heat of the solder given the atomic masses of Pb (207.2) and Sn (118.71).



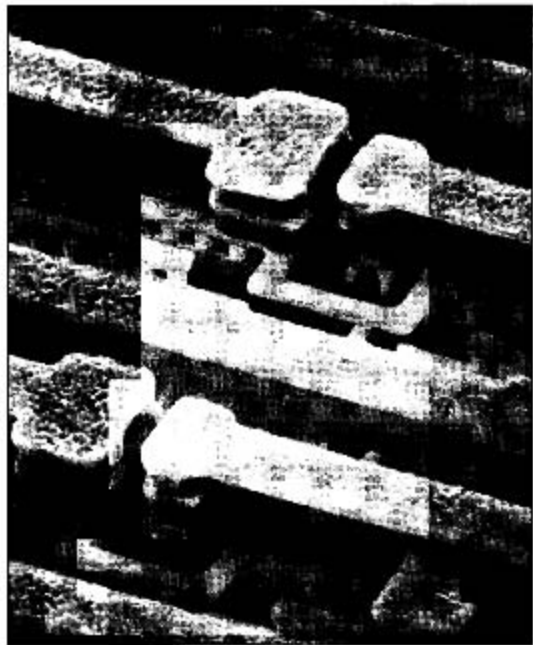
Walter Houser Brattain (1902–1987), one of the inventors of the transistor, looking at a vacuum evaporator used for depositing metal film electrodes on semiconductors (1937).

1. SOURCE: AIP Emilio Segrè Visual Archives, Brattain Collection.



Highly magnified scanning electron microscope (SEM) view of IBM's six-level copper interconnect technology in an integrated circuit chip. The aluminum in transistor interconnections in a silicon chip has been replaced by copper that has a higher conductivity (by nearly 40%) and also a better ability to carry higher current densities without electromigration. Lower copper interconnect resistance means higher speeds and lower RC constants [1997].

| SOURCE: Courtesy of IBM Corporation.



SEM view of three levels of copper interconnect metallization in IBM's new faster CMOS integrated circuits [1997].

| SOURCE: Courtesy of IBM Corporation.