# PART 1

# MATERIALS AND MECHANICAL DESIGN

# CHAPTER 1
# STRUCTURE OF SOLIDS

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## 1.1 INTRODUCTION

### 1.1.1 Effects of Structure on Properties

Physical properties of metals, ceramics, and polymers, such as ductility, thermal expansion, heat capacity, elastic modulus, electrical conductivity, and dielectric and magnetic properties, are a direct result of the structure and bonding of the atoms and ions in the material. An understanding of the origin of the differences in these properties is of great engineering importance.

In single crystals, a physical property such as thermal expansion varies with direction, reflecting the crystal structure; whereas in polycrystalline and amorphous materials, a property does not vary with direction, reflecting the average property of the individual crystals or the randomness of the amorphous structure. Most engineering materials are polycrystalline, composed of many grains, and thus an understanding of the properties requires not only a knowledge of the structure of the single grains but also a knowledge of grain size and orientation, grain boundaries, and other phases present; that is, a knowledge of the microstructure of this material.

### 1.1.2 Atomic Structure

Atoms consist of electrons, protons, and neutrons. The central nucleus consists of positively charged protons and electrically neutral neutrons. Negatively charged electrons are in orbits about the nucleus in different energy levels, occupying a much larger volume than the nucleus.

In an atom, the number of electrons equals the number of protons and, hence, an atom is neutral. The atomic number of an element is given by the number of protons, and the atomic weight is given by the total number of protons and neutrons. (The weight of the electrons is negligible.) Thus, hydrogen, H, with one proton and one electron, has an atomic number of 1 and an atomic weight of 1 and is the first element in the periodic chart. Oxygen, O, with atomic number 8, has eight protons and eight neutrons and, hence, an atomic weight of 16.

Completed electronic shells have a lower energy than partially filled orbitals when bonded to other atoms. As a result of this energy reduction, atoms share electrons to complete the shells, or gain or lose electrons to form completed shells. In the latter case, ions are formed in which the

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number of electrons is not equal to the number of protons. Thus, O by gaining two electrons, has a charge of −2 and forms the oxygen ion $O^{2-}$.

The periodic chart arranges elements in columns of the same electronic configuration. The first column consists of the alkalies Li, Na, K, Cs, Rb; each has one electron in the outer shell that can be lost. Similarly, the second column of alkaline-earths can form $Mg^{2+}$, $Ca^{2+}$, $Sr^{2+}$, $Ba^{2+}$ by losing two electrons. The seventh column consists of the halogens Fl, Cl, Br, I, which by gaining one electron become the halides, all with a charge of −1. The eighth column consists of the inert gases He, Ne, Ar, K, Xe, with completed shells. The bonding of the elements and ions with similar electronic configurations is similar. Moving down a column increases the number of electrons and, hence, the atom's size increases even though the outer electronic configuration remains the same.

The outer electrons that are lost, gained, or shared are called valence electrons, and the inner electrons are called core electrons. For the most part, the valence electrons are important in determining the nature of the bonding and, hence, the structure and properties of the materials.

### 1.1.3 Bonding

When two atoms or ions are within atomic distances of each other, distances of 0.5–3.0Å, bonding may occur between the atoms or ions. The resulting reduction in energy due to an attractive force leads to the formation of polyatomic gas molecules, liquids, and solids. If the energy of the bonds is large (75–275 kcal/mol), primary bonds are formed—metallic, ionic, or covalent. If the energy of the bond is smaller (1–10 kcal/mol), secondary bonds are formed—van der Waals and hydrogen. In addition, combinations of bond types, such as a mixture of ionic and covalent bonds, may occur.

#### Metallic Bonding

In a metallic crystal, an ordered arrangement of nuclei and their electrons is embedded in a cloud of valence electrons, which are shared throughout the lattice. The resulting bonding is a nondirectional primary bond. Since the binding energy of the valence electrons is relatively small, the mobility of these electrons is high and creates high electrical and thermal conductivity. The atoms are approximately spherical in shape as a result of the shape of completed inner shell. Examples of metals are Cu, Au, Ag, and Na.

#### Ionic Bonding

The strongest type of bonding between two oppositely charged particles is called ionic bonding. The positively charged ions (cations) attract as many negatively charged ions (anions) as they can and form ionic bonds. The primary bond formed is nondirectional if the bonding is purely ionic. $Li^+$ and $F^-$ in LiF form predominately ionic bonds. In general, since the electrons are strongly bonded, electrical and thermal conductivities are much smaller than in metals and, thus, ionic bonded materials are classified as insulators or dielectrics.

#### Covalent Bonding

Covalent bonding results from an overlap or sharing, not from gain or loss of valence electrons. A net reduction of energy as a result of each atom's completing the other's orbital also results in a primary bond, but it is directional. The directionality is a result of the shape of the orbitals involved in the bonding. When C is covalently bonded to four other C's in diamond, the bonding is purely covalent and the configuration of these four bonds is tetrahedral. When B, however, is bonded to three other B's, a triangular configuration is formed. Organic polymers and diatomic gases such as $Cl_2$ are typical examples of covalent bonding. As a result of the strong bonding of the valence electrons, these materials, for the most part, have low electrical and thermal conductivity.

#### Van der Waals and Hydrogen Bonding

Van der Waals bonds are secondary bonds, the result of fluctuating dipoles, due to the fact that at an instant of time the centers of positive and negative charge do not coincide. An example is an inert gas such as Ar, which below −190°C forms a solid as a result of these weak attractive forces. Similar weak forces exist in molecules and solids. Hydrogen bonds are also secondary bonds, but they are the result of permanent dipoles. For example, the water molecule, $H_2O$, is nonlinear and the bonding between H and an adjacent O in water results in $H_2O$ being a liquid above 0°C a 1 atm pressure rather than a gas, as is the case for other molecules of comparable molecular weight.

### 1.1.4 Simple Structures

If atoms or ions are considered to be spheres, then the most efficient packing of the spheres in space will form their most stable structure. However, the type of bonding—in particular, directional bonding—may affect the structure formed. In two dimensions, there is only one configuration that most efficiently fills space, the close-packed layer (see Fig. 1.1). If similar layers are stacked to form a three-dimensional structure, an infinite number of configurations is possible. Two are important. In

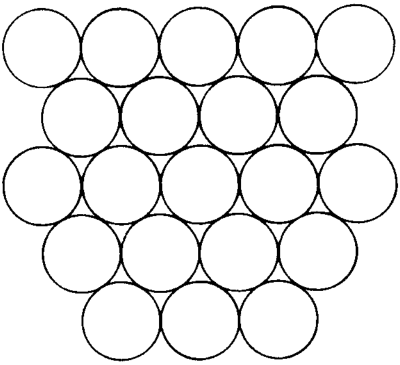

Fig. 1.1 Close-packed layer.

both, the first two layers are the same. In the first layer (*A*), the point at the center of three spheres provides a hollow for a fourth sphere to rest. A second close-packed layer (*B*) then can be placed on the first layer, with each sphere occupying the hollow. With the addition of a third layer to these two layers, two choices are possible. A sphere in the third layer can be placed above a sphere in the first layer in the spaces marked (•) in Fig. 1.2 or above a hollow not occupied by a sphere spaces marked (x) in the second layer. If the first stacking arrangement is continued, that is, the first and third layers in registry with each other (denoted *ABABA* . . .), the hexagonal close-packed (hcp) structure is generated, so called because of the hexagonal symmetry of the structure. If the second stacking arrangement is continued, that is, the first and third layers are not on top of each other (denoted *ABCABC* . . .), the cubic close-packed or face-centered cubic (fcc) structure is generated, so called because the structure formed is a face-centered cube. Both structures are shown in Fig. 1.3. In both structures, 74% of the volume is occupied and each sphere is contacted by 12 spheres (or 12 nearest neighbors), although the arrangement is different. Another common structure is the body-centered cubic (bcc) structure shown in Fig. 1.3. Here, each sphere has eight nearest neighbors, with another six at a slightly greater distance. The volume fraction occupied is 68%. In the hcp and fcc structures, the stacking of a fourth sphere on top of three in any close-packed layer generates a tetrahedral site or void, as shown in Fig. 1.4. Into such a site a smaller sphere with a coordination number of four could fit. Three spheres from each of two layers generate an octahedral site or void, as shown in Fig. 1.4. Into such a site a smaller sphere with a coordination number of six could fit. In the hcp and fcc structures, there are two tetrahedral and one octahedral sites per packing sphere; however, the arrangement of these sites is different.

### 1.1.5 Crystallography

All possible crystallographic structures are described in terms of 14 Bravais space lattices—only 14 different ways of periodically arranging points in space. These are shown in Fig. 1.5. Each of the

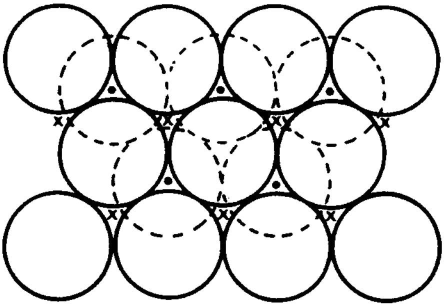

Fig. 1.2 Two possible sites for sphere in fcc and hcp structures: x and • (from D. M. Adams, *Inorganic Solids*, Wiley, New York, 1974).

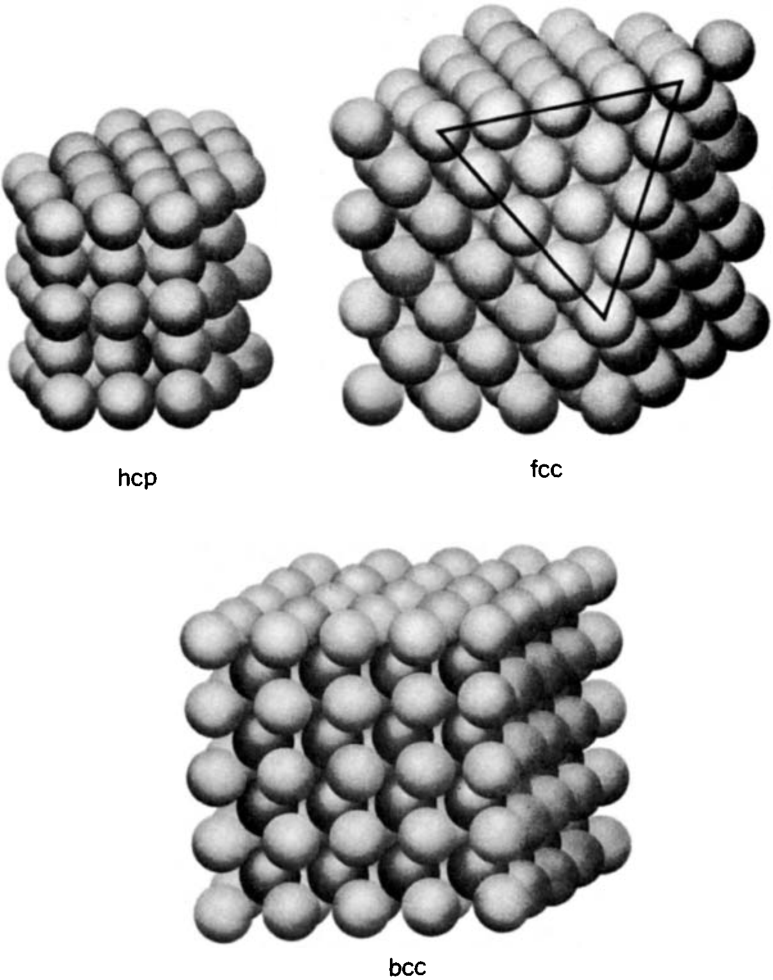

**Fig. 1.3** hcp, fcc, and bcc structures (from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials,* Wiley, New York, 1964, Vol. I, p. 51).

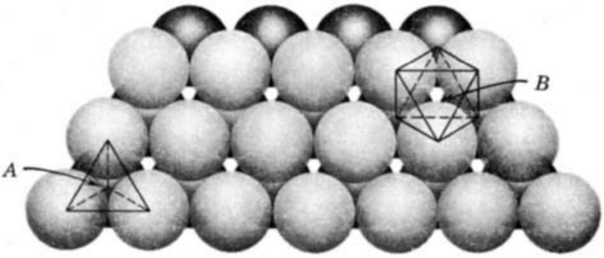

**Fig. 1.4** Tetrahedral and octahedral sites (from G. W. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials,* Wiley, New York, 1964, Vol. I, p. 58).

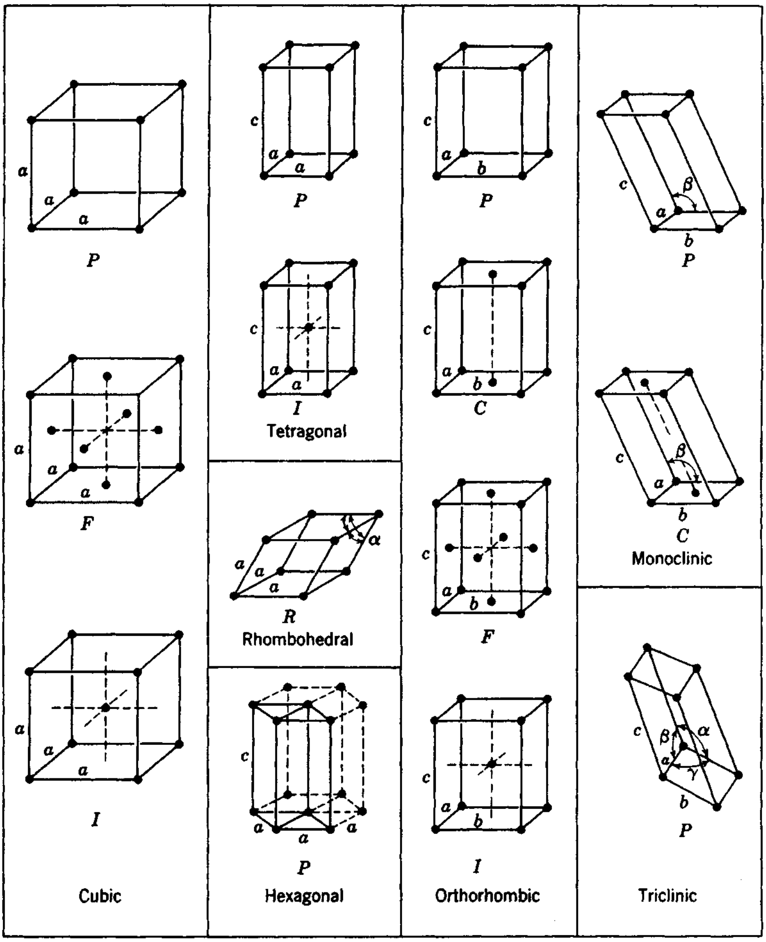

**Fig. 1.5** Bravais lattices (from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials,* Wiley, New York, 1964, Vol. I, p. 47).

positions in a given space lattice is equivalent and an atom or ion or group of atoms or ions can be centered on each position. Each of the lattices is described by a unit cell, as shown in Fig. 1.5. The seven crystallographic systems are also shown in Fig. 1.5.

### 1.1.6 States of Matter

Matter can be divided into gases, liquids, and solids. In gases and liquids, the positions of the atoms are not fixed with time, whereas in solids they are. Distances between atoms in gases are an order of magnitude or greater than the size of the atoms, whereas in solids and liquids closest distances between atoms are only approximately the size of the atoms. Almost all engineering materials are solids, either crystalline or noncrystalline.

#### Crystalline Solids

In crystalline solids, the atoms or ions occupy fixed positions and vibrate about these equilibrium positions. The arrangement of the positions is some periodic array, as discussed in Section 1.1.5. At 0°K, except for a small zero-point vibration, the oscillation of the atoms is zero. With increasing temperature the amplitude and frequency of vibration increase up to the melting point. At the melting point, the crystalline structure is destroyed, and the material melts to form a liquid. For a particular single crystal the external shape is determined by the symmetry of the crystal class to which it belongs. Most engineering materials are not single crystals but polycrystalline, consisting of many small crystals. These crystals are often randomly oriented and may be of the same composition or of different composition or of different structures. There may be small voids between these grains. Typical sizes of grains in such polycrystalline materials range from 0.01 to 10 mm in diameter.

### Noncrystalline Solids

Noncrystalline solids (glasses) are solids in which the arrangement of atoms is periodic (random) and lacks any long-range order. The external shape is without form and has no defined external faces like a crystal. This is not to say that there is no structure. A local or short-range order exists in the structure. Since the bonding between atoms or ions in a glass is similar to that of the corresponding crystalline solid, it is not surprising that the local coordination, number of neighbors, configuration, and distances are similar for a glass and crystal of the same composition. In fused $SiO_2$, for example, four O's surround each Si in a tetrahedral coordination, the same as in crystalline $SiO_2$.

Glasses do not have a definite melting point, crystals do. Instead, they gradually soften to form a supercooled liquid at temperatures below the melting point of the corresponding crystal. Glass formation results when a liquid is cooled sufficiently rapidly to avoid crystallization. This behavior is summarized in Fig. 1.6, where the volume $V$ is plotted as a function of temperature $T$.

## 1.1.7 Polymorphism

Crystalline materials of the same composition exhibit more than one crystalline structure called polymorphs. Fe, for example, exists in three different structures: $\alpha$, $\gamma$, and $\delta$ Fe. The $\alpha$ phase, ferrite, a bcc structure, transforms at 910°C to the $\gamma$ phase, austenite, an fcc structure, and then at 1400°C changes back to bcc structures $\delta$-iron or $\delta$-ferrite. The addition of C to Fe and the reactions and transformations that occur are extremely important in determining the properties of steel.

$SiO_2$ exhibits many polymorphs, including $\alpha$- and $\beta$-quartz, $\alpha$- and $\beta$-tridymite, and $\alpha$- and $\beta$-cristobalite. The $SiO_4$ tetrahedron is common to all the structures, but the arrangement or linking of these tetrahedra varies, leading to different structures. The $\alpha \rightarrow \beta$ transitions involve only a slight change in the Si–O–Si bond angle, are rapid, and are an example of a phase transformation called displacive. The quartz → tridymite → cristobalite transformations require the reformation of the new structure, are much slower than displacive transformations, and are called reconstructive phase transformations. The $\alpha \rightarrow \gamma \rightarrow \delta$ Fe transformations are other examples of reconstructive transformations.

A phase diagram gives the equilibrium phases a function of temperature, pressure, and composition. More commonly, the pressure is fixed at 1 atm and only the temperature and composition are varied. The Fe–C diagram is shown in Fig. 1.7.

## 1.1.8 Defects

The discussion of crystalline structures assumes that the crystal structures are perfect, with each site occupied by the correct atoms. In real materials, at temperatures greater than 0°K, defects in the crystalline structure will exist. These defects may be formed by the substitution of atoms different from those normally occupying the site, vacancies on the site, atoms in sites not normally occupied (interstitials), geometrical alterations of the structure in the form of dislocations, twin boundaries, or grain boundaries.

### Solid Solution

When atoms or ions are approximately the same size, they may substitute for another in the structure. For example, Cu and Au have similar radii and at high temperature form a complete solid solution,

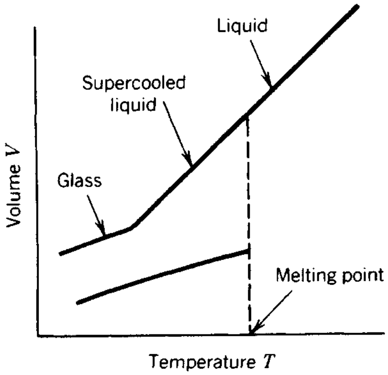

Fig. 1.6 Glass formation.

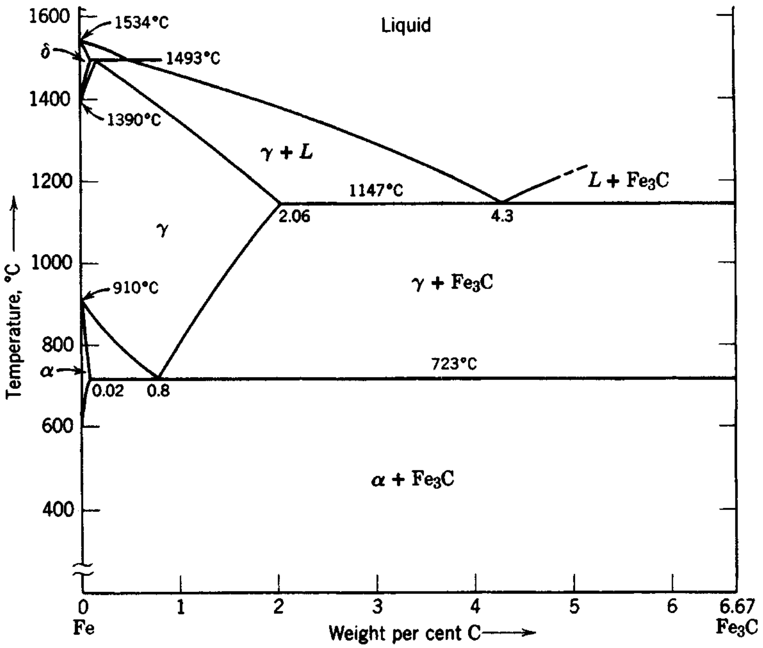

**Fig. 1.7** Fe–C phase diagram (from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials,* Wiley, New York, 1964, Vol. I, p. 185).

as shown in Fig. 1.8. A ceramic example is the $Cr_2O_3$–$Al_2O_3$ system shown in Fig. 1.9, where Cr and Al substitute for each other. $Cr^{3+}$ has a radius of 0.76 Å and Al has a radius of 0.67 Å. Complete solid solution is not possible if the size difference between atoms or ions is too large, if the structures of the end members are different, or if there are charge differences between ions being substituted. In the last case, substitution is possible only if the charge is compensated for by the creation of vacancies or by oxidation or reduction of ions.

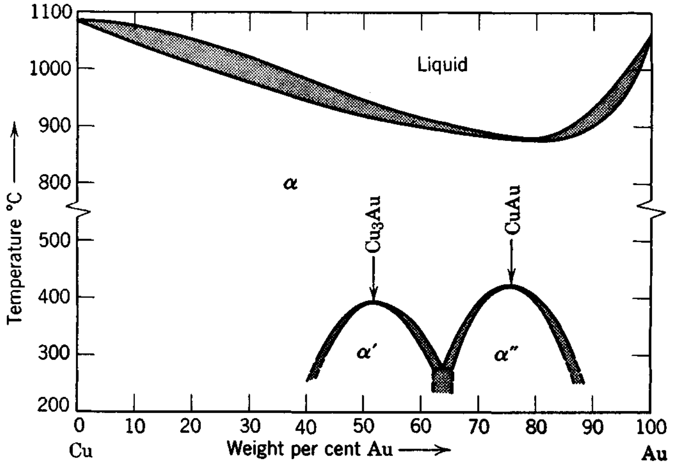

**Fig. 1.8** Cu–Au system (from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials,* Wiley, New York, 1964, Vol. I, p. 230).

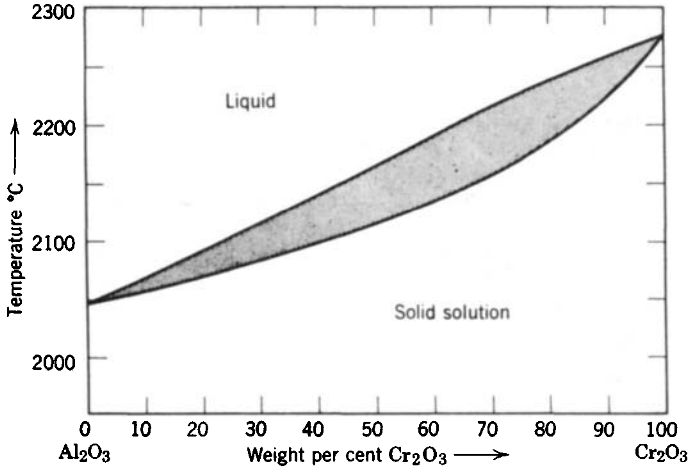

**Fig. 1.9** $Cr_2O_3$-$Al_2O_3$ system (from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials,* Wiley, New York, 1964, Vol. I, p. 229).

### Point Defects

For single-atom structures, a number of point defects are illustrated in Fig. 1.10. Shown are a vacancy (an absent atom); an interstitial atom, occupying a normally unoccupied site; and two types of impurities, one in an interstitial site and the other substituting for an atom. In Fig. 1.11 a number of point defects are shown for an ionic compound *AB*. Substitutional ions, vacancies, and impurity ions are shown. In ionic compounds, because charges must be balanced, when a cation is removed, an anion is also removed. The resulting vacancy and interstitial point defects are called a Schottky pair. A Frenkel defect occurs when an ion is removed from its normal site and is placed in an interstitial site. The presence of defects—interstitials and vacancies—is necessary for diffusion to occur in many crystalline solids.

### Dislocations

Two basic types of dislocations exist in solids—edge and screw dislocations. An edge dislocation consists of an extra plane of atoms, as shown in Fig. 1.12. It is represented by the symbol $\perp$ and has associated compression and tension. A screw dislocation is formed by the atom planes spiraling

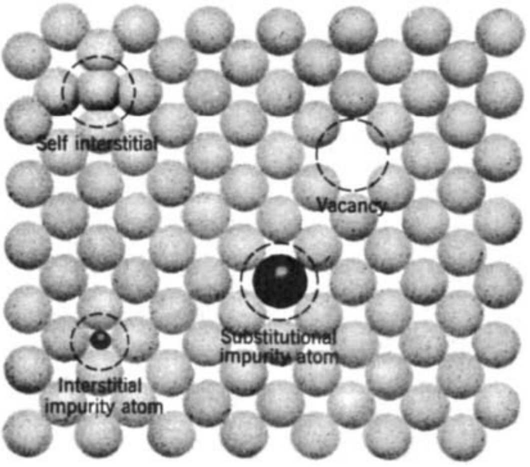

**Fig. 1.10** Point defects (from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials,* Wiley, New York, 1964, Vol. I, p. 77).

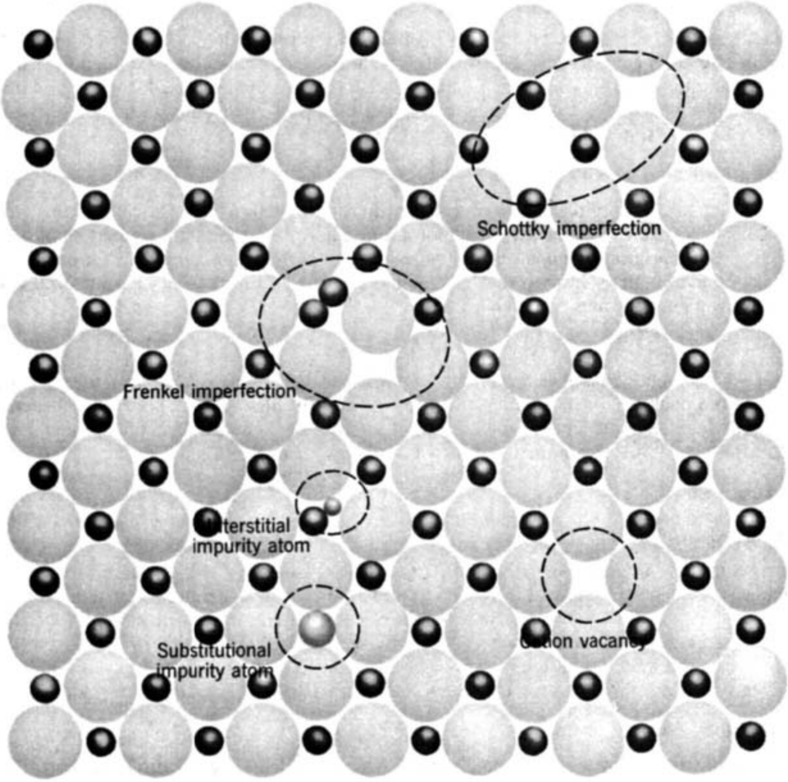

**Fig. 1.11** Point defects in a compound *AB* (from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials,* Wiley, New York, 1964, Vol. I, p. 78).

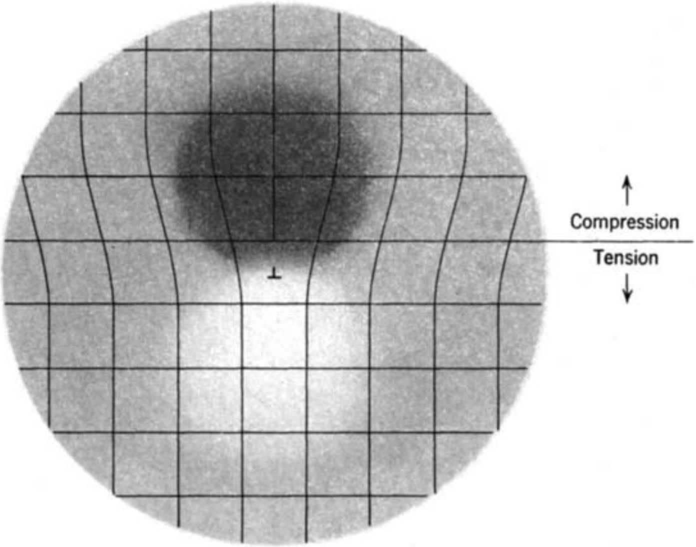

**Fig. 1.12** Edge dislocation (from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials,* Wiley, New York, 1964, Vol. I, p. 85).

and is shown in Fig. 1.13. Combinations of screw and edge dislocations also exist, which are called mixed dislocations.

Dislocations are important because of their effect on the properties, in particular the mechanical properties, of engineering materials. The slip of a metal is the result of the movement of dislocations; plastic deformation is the result of the generation of dislocations; the increased strength and brittleness as a result of cold working is due to a generation and pileup of dislocations; and creep in a material is the result of dislocation climb.

### Grain Boundaries

Grain boundaries are the regions that occur when there is no alignment between grains in a polycrystalline material. Grain boundaries are important in determining the bulk properties of a material. Impurities segregate at grain boundaries if they reduce the surface energy. Diffusion is usually faster along grain boundaries than through the bulk of the material. Deformation of a material can occur by relative movement of grains.

## 1.2 METALS

Most elements are metals, many of which are important technologically. The structure of metals can be considered the packing of the spheres that most efficiently fills space. Three basic structures will be considered: face-centered cubic (fcc), hexagonal close-packed (hcp), and body-centered cubic (bcc). An introductory discussion of these structures is given in Section 1.1.4.

### 1.2.1 Structures

### Face-Centered Cubic (fcc)

The fcc structure is shown in Fig. 1.3. The *ABCABC* . . . layers, of which there are four sets, are perpendicular to the body diagonals of the cube. The 12 nearest neighbors at a distance $D$ (the diameter of a sphere) form a cubo-octahedron about each sphere, as shown in Fig. 1.14. There are six next nearest neighbors at a distance $\sqrt{2}\,D$ and 24 third-nearest neighbors at a distance $\sqrt{3}\,D$. The symmetry of the structure is cubic $F$ in Fig. 1.5. The following metals adopt the fcc structures as one of their polymorphs: Al, Ca, Fe, Co, Ni, Cu, Sr, Y, Rh, Pd, Ag, Ir, Pt, Au, and Pb.

### Hexagonal Close-Packed (hcp)

The hcp structure is shown in Fig. 1.3. There is only one close-packed direction with a packing sequence *ABAB* . . . The hexagonal symmetry is shown in Fig. 1.5. As in the fcc structure, there are 12 nearest neighbors, but their configuration is different in the form of a twinned cubooctahedron, as shown in Fig. 1.14. There are six next nearest neighbors, as in the fcc structure, but only two third-nearest neighbors at a distance $\sqrt{8/3}\,D$ or $1.633D$, the distance from one sphere to the spheres

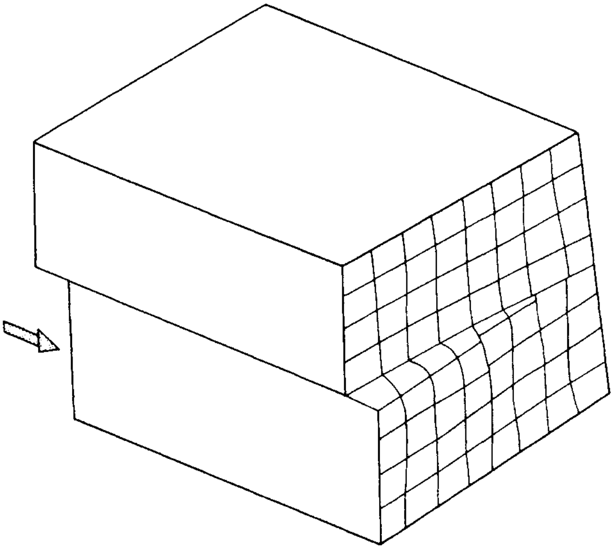

**Fig. 1.13** Screw dislocation (from W. D. Kingery, H. K. Bowen, and D. R. Uhlmann, *Introduction to Ceramics*, Wiley, New York, 1976).

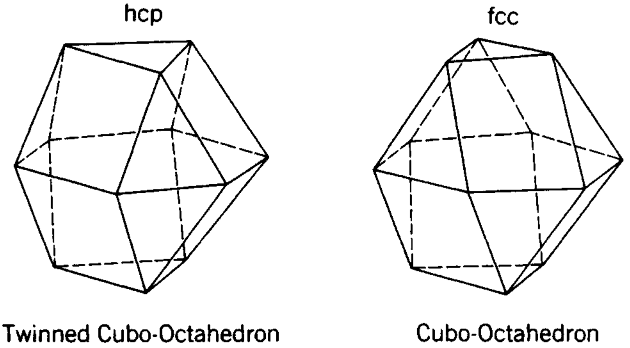

**Fig. 1.14** Configuration of nearest neighbors in hcp and fcc structures (from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials,* Wiley, New York, 1964.

in the second layer above or below the given sphere. The $c/a$ ratio $= 1.633$ is defined in Fig. 1.5 for the hexagonal lattice. If the shape of the atoms is ellipsoidal rather than spherical, then the $c/a$ ratio deviates from the 1.633 value. Metals with the hcp structure and their $c/a$ ratio are given in Table 1.1.

### Body-Centered Cubic (bcc)

The bcc structure is shown in Fig. 1.3. There, the distance of the next nearest neighbors is close to the nearest-neighbor distance. Thus, the effective coordination number is 14, comparable to the fcc and hcp structures. Metals that have the bcc structure are Li, Na, K, Ca, V, Ti, Cr, Fe, Rb, Sr, Nb, Mo, Cs, Ba, Hf, Ta, and W.

The structure of a particular metal adopts cannot be explained only in terms of volume occupied or number of nearest neighbors. The energy differences between fcc, hcp, and bcc structures are very small. The nature of the bonding and the electronic configuration also play important roles.

## 1.2.2 Alloys

The addition of a second element (or more) to a metal results in an alloy, which may have improved engineering properties. Some examples of alloys are given in Table 1.2. The extent of solid solution and phases formed is given by the appropriate phase diagram. The extent of solid solution is determined by the relative sizes of the atoms.

## 1.2.3 Noncrystalline Metals

Noncrystalline or amorphous metals can be prepared in the form of ribbon or film by rapid quenching techniques (cooling rate $> 10^5$ deg/sec), such as splat cooling or vapor, electrolytic, or chemical deposition. Compositions include a metal and metalloid, such as Si, Ge, P, Sb, or C, with generally 80 wt% metal. Typical compositions are $Ni_3P$, $Au_3Si$ and Pd–Fe–Si. The structure of these materials consists of a dense, random packing of the metal in which approximately 64% of the volume is occupied and in which the metalloid occupies irregularly shaped tetrahedra, octahedra, and other sites and stabilizes the structure. Improved mechanical properties, including higher strengths, greater ductility, improved corrosion resistance, and interesting magnetic properties, make these promising engineering materials.

**Table 1.1 hcp Metals**

| Metal | $c/a$ | Metal | $c/a$ |
|---|---|---|---|
| Be | 1.568 | Y | 1.571 |
| Na | 1.63 | Zr | 1.593 |
| Mg | 1.623 | Ru | 1.582 |
| Sc | 1.594 | Cd | 1.886 |
| Co | 1.623 | Hf | 1.581 |
| Zn | 1.856 | Re | 1.615 |
| Sr | 1.63 | Os | 1.579 |

**Table 1.2 Alloys**

| Name | Composition |
|---|---|
| Monel | Cu–Ni |
| Bronze | Cu–Sn |
| Steel | Fe–C ($C < 2\%$) |
| Cast iron | Fe–Si–C ($2\% < Si < 4\%$) |
| Brass | Cu–Zn |

## 1.3 CERAMICS

Ceramics are nonmetallic inorganic materials. Thus, the oxides of all metals such as $Fe_2O_3$, $TiO_2$, $Al_2O_3$, and $SiO_2$ and materials such as diamond, SiN, SiC, and Si are considered to be ceramics.

### 1.3.1 Crystalline Ceramics

Most oxides can be considered close packings of oxygen ions with the cations occupying the tetrahedral and/or octahedral sites in the structure. As an example, $\alpha$-alumina ($\alpha$-$Al_2O_3$) consists of an hcp packing of $O^{2-}$ with two thirds of the octahedral sites occupied by $Al^{3+}$ in an orderly fashion. Since for each $O^{2-}$ there exist one octahedral and two tetrahedral sites, in $Al_2O_3$ there would be three octahedral sites in which two $Al^{3+}$ are placed thus two-thirds of the octahedral and none of the tetrahedral sites are filled. The compound is electrically neutral, since $2 \times (3+)$ (Al) $= 3 \times (2-)$ (O). If the Al is shared by six O's, then $\frac{3}{6} = \frac{1}{2}$ of its charge is contributed to each O. For the charge on each O to be satisfied, four Al's need to be coordinated to each O, since $4(\frac{1}{2}) = 2$. A notation to indicate the coordination scheme for $\alpha$-$Al_2O_3$ is 6:4—each Al is coordinated to six O's and each oxygen is coordinated to four Al's.

A summary of common ceramic structures is given in Table 1.3. The structure of silicates is complicated, but the basic unit is the $SiO_4$ tetrahedron. The three polymorphs of $SiO_2$—quartz, tridymite and cristobalite—have different arrangements for the linking of all four vertices of the tetrahedron. Each Si is bonded to four O's and each O is bonded to two Si's. In the layer silicates such as micas, clays, and talc, only three of the vertices are linked. The result is a laminar structure in which the bonding between layers is a weaker ionic bonding, hydrogen bonding, or van der Waals bonding, respectively, for mica, clay, and talc.

Of particular importance in semiconductors is the diamond structure. In this structure, each atom is tetrahedrally coordinated to four other atoms. The predominant covalent bonding of the structure is manifested by the high degree of directionality in the bonding. In addition to diamond, Si and Ge have this structure, as do other semiconductors that have been doped with other elements.

### 1.3.2 Noncrystalline Ceramics

Common glass compositions are fused $SiO_2$, soda–lime silica, soda–borosilicate, and alkali–lead silicate. Glass formers such as $SiO_2$ and $B_2O_3$ are characterized by a high viscosity at the melting point and readily form glasses when cooled. Network modifiers such as $Na_2O$ and CaO do not form glasses unless quenched at extremely high rates. Intermediaries such as $Al_2O_3$ and PbO, while not readily forming glasses by themselves, can be present in high concentrations when combined with glass formers.

Amorphous or fused $SiO_2$ has Si tetrahedrally coordinated to four O's, with each O bonded to two Si's. Thus, $SiO_4$ tetrahedra are linked, sharing all four vertices in a continuous three-dimensional network. The structure has short-range order but no long-range order. The introduction of network modifiers results in the formation of nonbridging oxygen—oxygen bonded to only one Si and thus

**Table 1.3 Common Ceramic Structures**

| Structure | Examples | Coordination | Packing of Anion |
|---|---|---|---|
| Rock salt | MgO, CaO, SrO, FeO | 6 : 6 | fcc |
| Zincblende | SiC | 4 : 4 | ccp |
| Rutile | $TiO_2$, $GeO_2$ | 6 : 3 | Distorted hcp |
| Perovskite | $SrTiO_3$, $BaTiO_3$ | 12 : 6 : 6 | fcc |
| Spinel | $MgAl_2O_4$, $FeAl_2O_4$ | 4 : 6 : 4 | fcc |
| Corundum | $\alpha$-$Al_2O_3$, $Fe_2O_3$ | 6 : 4 | hcp |
| Fluorite | $UO_2$, $ZrO_2$ | 8 : 4 | Simple cube |

negatively charged. The cation, such as $Na^+$, is in the interstitial sites balancing the charge. The result is an increase in density, a large decrease in viscosity, and a decrease in thermal expansion with increasing alkali content. The alkaline earths behave in a similar manner. Commercial soda–lime–silica glass (72 wt% $SiO_2$, 12–15 wt% $Na_2O$, 10–15 wt% CaO) has a broken up silica network with Na and Ca ions in large interstitials.

### 1.3.3 Glass–Ceramics

Glass–ceramics are materials that have been fabricated as glasses and then crystallized as a result of controlled nucleation and growth. In most cases, nucleating agents such as $TiO_2$, $P_2O_5$, Pt, or $ZrO_2$ are added to aid in crystallization. The microstructure of many glass–ceramics consists of 95–98% crystalline phase with a grain size $< 1\ \mu m$ embedded in a small amount of a pore-free glassy phase. Typical composition systems are $Li_2O$–$Al_2O_3$–$SiO_2$, and $Na_2O$–BaO–$Al_2O_3$–$SiO_2$. Some of the desirable properties of various glass–ceramic systems are zero or very low thermal expansion, high mechanical strength, high electrical resistivity, and machinability.

## 1.4 POLYMERS

Polymers are organic materials that consist of chains of C and H. The intrachain bonding is covalent, while the interchain bonding is van der Waals. The repeating structural units, monomers, are linked together to form the polymer.

Isomers are organic compounds of the same composition but with a different arrangement of the atoms. Copolymerization is the process of linking different polymers together. Many polymers are noncrystalline because the long chains become entangled or because of side groups attached to the chain, particularly if they are large or irregularly placed. Both of these factors make it difficult to crystallize the chains. The addition of plasticizers—low-molecular-weight compounds that separate the chains—also help prevent crystallization.

The manner in which the polymers are formed affects the final structure. Bifunctional monomers result in two bonds that form linear chains, whereas trifunctional or tetrafunctional monomers result in network or framework polymers. This results in cross linking and in increased structural rigidity and less elasticity. The shape of the linear polymers can be altered by the addition of side groups; not only does the packing become less ordered, but the interbonding becomes stronger. Branching, the splitting of the polymer chain, is another way to introduce three dimensions into the polymer structure.

Since polymers are organic materials when compared to metals and ceramics, they tend to have low melting or softening temperatures and are flammable. The elastic moduli are lower by several orders of magnitude and they serve as electrical insulators.

## 1.5 COMPOSITES AND COATINGS

Many modern engineering materials have been developed by combining two or more materials into a single material, a composite, or by coating one material with another. The structure of such composites and coating will be discussed in general, but the specifics will not be covered.

### 1.5.1 Fiberglass

Fiberglass is formed from glass fibers impregnated in an order or random manner in a plastic material. The fibers are usually of a composition known as E-glass ($SiO_2$, 54 wt%; $Al_2O_3$, 14 wt%; $B_2O_3$, 10 wt%; MgO, 4.5 wt%; and CaO, 17.5 wt%), are typically 0.00023–0.00053 in. in diameter, and woven together to form continuous fibers or to form cloth.

### 1.5.2 Coatings

Various coatings used in engineering applications are summarized in Table 1.4. Coatings can serve as a protective layer for the substrate and/or alter the appearance of the surface. The structures of the coating and the substrate have previously been discussed. Of great importance is the bonding structure at the interface between the coating and the substrate.

In general, the bonding will be affected by atomistic and microscopic considerations of the surfaces. The bonding in the material, whether metallic, ionic, or covalent, may be continued or altered

**Table 1.4 Coatings**

| Coating | Composition | Substrate |
|---|---|---|
| Enamel | Inorganic glass | Metal |
| Glaze | Inorganic glass | Ceramic |
| Paint | Organic | Metal, polymer |
| Galvanized and plating | Metal | Metal |

in the interface. Such factors as surface roughness, porosity, and oxidation/reduction, and the presence of impurities, will affect the bonding at the interface.

Enamels are used on metals to protect the surface from oxidation and to change the color and appearance of the surface. The vitreous enamel is fused to the surface of the metal. The bonding changes from metallic to ionic–covalent on the enamel. The thermal expansion of the enamel is usually less than that of the metal substrate, so that the enamel surface is in compression, thus improving the mechanical properties of the enamel. Glazes are used to decrease the porosity of the ceramic substrate and to alter the appearance of the surface.

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