



Class: 1st

Subject: Engineering Materials

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Crystallographic Directions and Plains

Atomic Radius versus Lattice Parameter: Directions in the unit cell along which atoms are in continuous contact are close-packed directions. In simple structures, particularly those with only one atom per lattice point, we use these directions to calculate the relationship between the apparent size of the atom and the size of the unit cell. Geometrically determining the length of the direction relative to the lattice parameters, and then adding the number of atomic radii along this direction, we can determine the desired relationship. Example 2 illustrates how the relationships between lattice parameters and atomic radius are determined.

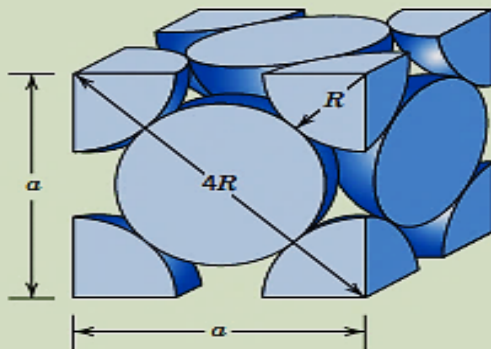
EXAMPLE.1

Determination of FCC Unit Cell Volume

Calculate the volume of an FCC unit cell in terms of the atomic radius R .

Solution

In the FCC unit cell illustrated,



the atoms touch one another across a face-diagonal the length of which is $4R$. Since the unit cell is a cube, its volume is a^3 , where a is the cell edge length. From the right triangle on the face,

$$a^2 + a^2 = (4R)^2$$

or, solving for a ,

$$a = 2R\sqrt{2}$$

The FCC unit cell volume V_C may be computed from

$$V_C = a^3 = (2R\sqrt{2})^3 = 16R^3\sqrt{2}$$

Coordination Number: The coordination number is the number of atoms touching a particular atom, or the number of nearest neighbors for that particular atom. This is one indication of how tightly and efficiently atoms are packed together. For ionic solids, the coordination number of cations is defined as the number of nearest anions. The coordination number of anions is the number of nearest cations. In cubic structures containing only one atom per lattice point, atoms have a coordination number related to the lattice structure. By inspecting the unit cells in figure 3, we see that each atom in the **SC** structure has a coordination number of six, while each atom in the **BCC** structure has eight nearest neighbors. Later, we will show that each atom in the **FCC** structure has a coordination number of 12, which is the maximum.

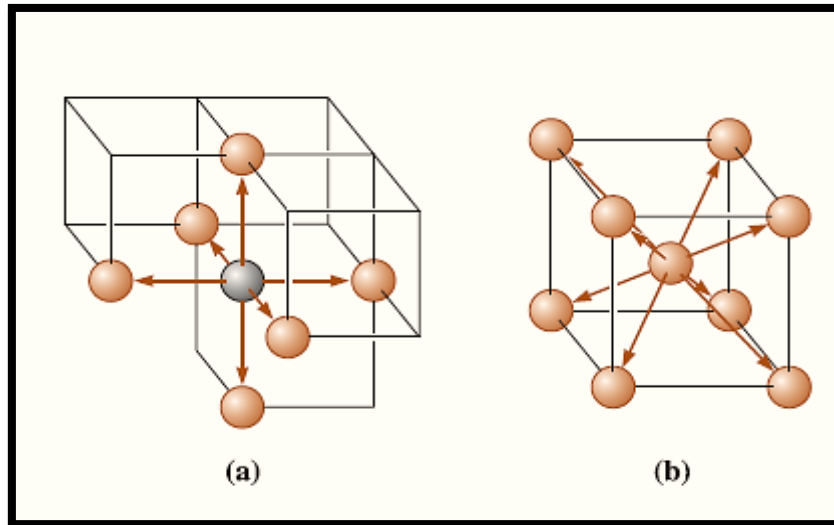


Figure 1. Illustration of coordinations in (a) SC and (b) BCC unit cells. Six atoms touch each atom in SC, while eight atoms touch each atom in the BCC unit cell.

Atomic Packing Factor (APF): The packing factor is the fraction of space occupied by atoms, assuming that atoms are hard spheres sized so that they touch their closest neighbor. The general expression for the packing factor is:

$$\text{APF} = \frac{(\text{number of atoms/unit cell}) \cdot (\text{volume of each atom})}{\text{volume of unit cell}}$$

EXAMPLE.2 Calculating the Packing Factor.

Calculate the atomic packing factor for the FCC cell.

SOLUTION

In a FCC cell, there are four lattice points per cell; if there is one atom per lattice point, there are also four atoms per cell. The volume of one atom is $\frac{4\pi r^3}{3}$ and the volume of the unit cell is a_0^3 .

$$\text{Packing factor} = \frac{(4 \text{ atoms/cell}) \left(\frac{4}{3}\pi r^3\right)}{a_0^3}$$

Since, for FCC unit cells, $a_0 = 4r/\sqrt{2}$:

$$\text{Packing factor} = \frac{(4) \left(\frac{4}{3}\pi r^3\right)}{(4r/\sqrt{2})^3} = \frac{\pi}{\sqrt{18}} \cong 0.74$$

The packing factor of $\pi/\sqrt{18} \cong 0.74$ in the FCC unit cell is the most efficient packing possible. BCC cells have a packing factor of 0.68 and SC cells have a packing factor of 0.52. Notice that the packing factor is independent of the radius of atoms, as long as we assume that all atoms have a fixed radius.



The FCC arrangement represents a close-packed structure (CP) (i.e., the packing fraction is the highest possible with atoms of one size). The SC and BCC structures are relatively open. We will see later that it is possible to have a hexagonal structure that has the same packing efficiency as the FCC structure. This structure is known as the hexagonal close-packed structure (HCP). Metals with only metallic bonding are packed as efficiently as possible. Metals with mixed bonding, such as iron, may have unit cells with less than the maximum packing factor. No commonly encountered engineering metals or alloys have the SC structure, although this structure is found in ceramic materials.

Density: The theoretical density of a material can be calculated using the properties of the crystal structure. The general formula is:

$$\text{Density } (\rho) = \frac{(\text{number of atoms/unit cell})(\text{atomic mass})}{(\text{volume of unit cell})(\text{Avogadro's number})}$$

If a material is ionic and consists of different types of atoms or ions, this formula will have to be modified to reflect these differences. Example.4 illustrates how to determine the density of BCC iron.

EXAMPLE.3 Determining the Density of BCC Iron

Determine the density of BCC iron, which has a lattice parameter of **0.2866 nm**.

SOLUTION

For a BCC cell,

$$\text{Atoms/cell} = 2$$

$$a_0 = 0.2866 \text{ nm} = 2.866 \times 10^{-8} \text{ cm}$$

$$\text{Atomic mass of iron} = 55.847 \text{ g/mol}$$

$$\text{Volume of unit cell} = a_0^3 = (2.866 \times 10^{-8} \text{ cm})^3 = 23.54 \times 10^{-24} \text{ cm}^3/\text{cell}$$

$$\text{Avogadro's number } N_A = 6.02 \times 10^{23} \text{ atoms/mol}$$

$$\text{Density } \rho = \frac{(\text{number of atoms/cell})(\text{atomic mass of iron})}{(\text{volume of unit cell})(\text{Avogadro's number})}$$

$$\rho = \frac{(2)(55.847)}{(23.54 \times 10^{-24})(6.02 \times 10^{23})} = 7.882 \text{ g/cm}^3$$

The measured density is 7.870 g/cm^3 . The slight discrepancy between the theoretical and measured densities is a consequence of defects in the material. As mentioned before, the term “defect” in this context means imperfections with regard to the atomic arrangement.

The Hexagonal Close-Packed Structure: A special form of the hexagonal structure, the hexagonal close-packed structure (HCP), is shown in figure 2. The unit cell is the skewed prism, shown separately. The HCP structure has one lattice point per cell (one from each of the eight corners of the prism) but two atoms are associated with each lattice point. One atom is located at a corner, while the second is located within the unit cell. Thus, the basis is 2.

In metals with an ideal HCP structure, the a_0 and c_0 axes are related by the ratio $c_0 = a_0 = 1.633$. Most HCP metals, however, have c_0 / a_0 ratios that differ slightly from the ideal value because of mixed bonding. Because the HCP structure, like the FCC structure, has the most efficient packing factor of **0.74** and a coordination number of **12**, a number of metals possess this structure. Table (1) summarizes the characteristics of crystal structures of some metals.

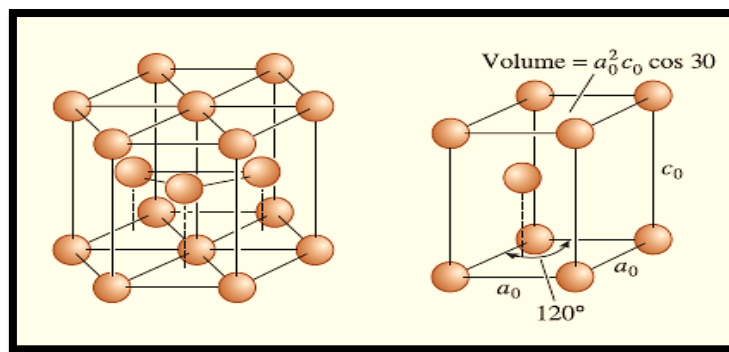


Figure 2. The hexagonal close packed (HCP) structure (left) and its unit cell.

Table 1. Crystal structure characteristics of some metals

Structure	a_0 versus r	Atoms per Cell	Coordination Number	Packing Factor	Examples
Simple cubic (SC)	$a_0 = 2r$	1	6	0.52	Polonium (Po), α -Mn
Body-centered cubic	$a_0 = 4r/\sqrt{3}$	2	8	0.68	Fe, Ti, W, Mo, Nb, Ta, K, Na, V, Zr, Cr
Face-centered cubic	$a_0 = 4r/\sqrt{2}$	4	12	0.74	Fe, Cu, Au, Pt, Ag, Pb, Ni
Hexagonal close-packed	$a_0 = 2r$ $c_0 \approx 1.633a_0$	2	12	0.74	Ti, Mg, Zn, Be, Co, Zr, Cd

Structures of ionically bonded materials can be viewed as formed by the packing (cubic or hexagonal) of anions. Cations enter into the interstitial sites or holes that remain after the packing of anions.

Allotropic or Polymorphic Transformations

Materials with more than one crystal structure at different temperature are called **allotropic** or **polymorphic**. The term allotropy is normally reserved for this behavior in pure elements, while the term polymorphism is used for compounds. You may have noticed in Table 2 that some metals, such as **iron** and **titanium**, have more than one crystal structure. At low temperatures, iron has the BCC structure, but at higher temperatures, iron transforms to an FCC structure. These transformations result in changes in properties of materials and form the basis for the heat treatment of steels and many other alloys.



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Many ceramic materials, such as silica (SiO₂) and zirconia (ZrO₂), also are polymorphic. A volume change may accompany the transformation during heating or cooling; if not properly controlled, this volume change causes the ceramic material to crack and fail.

Polymorphism is also of central importance to several other applications. The properties of some materials can depend quite strongly on the type of polymorph. For example, the dielectric properties of such materials as PZT and BaTiO₃ depend upon the particular polymorphic form.

EXAMPLE.4 Calculating Volume Changes in Polymorphs of Zirconia (ZrO₂)

Calculate the percent volume change as zirconia (ZrO₂) transforms from a tetragonal to a monoclinic structure. The lattice constants for the monoclinic unit cells are: [(**a = 5.156**), (**b = 5.191**), and (**c = 5.304**)] Å°, respectively. The angle **b** for the monoclinic unit cell is (**98.9°**). The lattice constants for the tetragonal unit cell are [(**a = 5.094**) and (**c = 5.304**)] Å°, respectively. Does the zirconia expand or contract during this transformation? What is the implication of this transformation on the mechanical properties of zirconia ceramics ?

SOLUTION

The volume of a tetragonal unit cell is given by $V = a^2c = (5.094)^2(5.304) = 134.33 \text{ \AA}^3$.

The volume of a monoclinic unit cell is given by $V = abc \sin \beta = (5.156)(5.191)(5.304) \sin(98.9) = 140.25 \text{ \AA}^3$.

Thus, there is an expansion of the unit cell as ZrO₂ transforms from a tetragonal to monoclinic form.

The percent change in volume = (final volume – initial volume)/(initial volume) * 100 = (140.25 – 134.33 Å³)/134.33 Å³ * 100 = 4.21%.

Points, Directions, and Planes in the Unit Cell

Coordinates of Points: We can locate certain points, such as atom positions, in the lattice or unit cell by constructing the right-handed coordinate system in figure 3. Distance is measured in terms of the number of lattice parameters we must move in each of the x, y, and z coordinates to get from the origin to the point in question. The coordinates are written as the three distances, with commas separating the numbers.

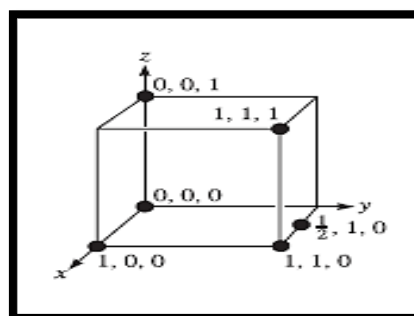


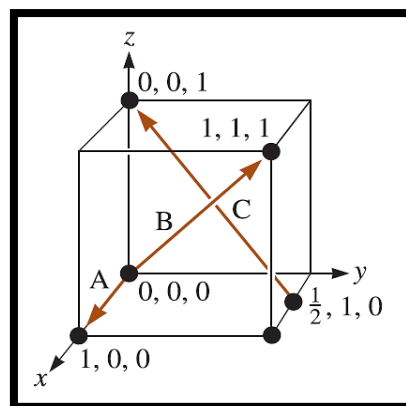
Figure 3. Coordinates of selected points in the unit cell. The number refers to the distance from the origin in terms of lattice parameters.

Directions in the Unit Cell: Certain directions in the unit cell are of particular importance. Miller indices for directions are the shorthand notation used to describe these directions. The procedure for finding the Miller indices for directions is as follows:

1. Using a right-handed coordinate system, determine the coordinates of two points that lie on the direction (**Intercept**).
2. Subtract the coordinates of the “tail” point from the coordinates of the “head” point to obtain the number of lattice parameters traveled in the direction of each axis of the coordinate system (**Reciprocals**).
3. Clear fractions and/or reduce the results obtained from the subtraction to lowest integers (**Reduction**).
4. Enclose the numbers in square brackets []. If a negative sign is produced, represent the negative sign with a bar over the number (**Enclosure**).

EXAMPLE.5 Determining Miller Indices of Directions

Determine the Miller indices of directions A, B, and C in figure below.



SOLUTION

Direction A

1. Two points are 1, 0, 0, and 0, 0, 0
2. $1, 0, 0 - 0, 0, 0 = 1, 0, 0$
3. No fractions to clear or integers to reduce
4. [100]

Direction B

1. Two points are 1, 1, 1 and 0, 0, 0
2. $1, 1, 1 - 0, 0, 0 = 1, 1, 1$
3. No fractions to clear or integers to reduce
4. [111]

Direction C

1. Two points are 0, 0, 1 and $\frac{1}{2}, 1, 0$
2. $0, 0, 1 - \frac{1}{2}, 1, 0 = -\frac{1}{2}, -1, 1$
3. $2(-\frac{1}{2}, -1, 1) = -1, -2, 2$
4. $[\bar{1}\bar{2}2]$

Inter atomic Bonding

There are four important mechanisms by which atoms are bonded in engineered materials. These are:

1. Metallic bond.
2. Covalent bond.
3. Ionic bond.
4. Van der Waals bond.

In the first three of these mechanisms, bonding is achieved when the atoms fill their outer s and p levels. These bonds are relatively strong and are known as primary bonds (relatively strong bonds between adjacent atoms resulting from the transfer or sharing of outer orbital electrons). The van der Waals bonds are secondary bonds and originate from a different mechanism and are relatively weaker.

1.The Metallic Bond: It is the atomic bonding mechanism in pure metals and metal alloys. The metallic bond forms when atoms give up their valence electrons, which then form an electron sea. The positively charged atom cores are bonded by mutual attraction to the negatively charged electrons.

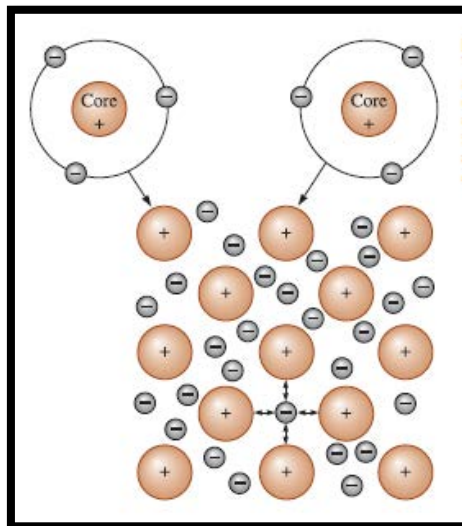


Figure 1. Diagrammatic Representation of the "Metallic Bond".

Because their valence electrons are not fixed in any one position, most pure metals are good electrical conductors of electricity at relatively low temperatures ($T < 300 \text{ K}$). Under the influence of an applied voltage, the valence electrons move, causing a current to flow if the circuit is complete. Because of the general distribution of electrons and their freedom to move within the metal, metallic bonding provides typical properties of materials characterized such as good electrical conductivity, good conduction of heat and good ductility.

2.The Covalent Bond: In the covalent bond, electrons are shared (as opposed to transferred) between atoms in their outermost shells to achieve a stable set of eight. For example, a silicon atom, which has a valence of four, gets eight electrons in its outer energy shell by sharing its electrons with four surrounding silicon atoms (Figure 2). Each instance (case) of sharing represents one covalent bond; thus, each silicon atom is bonded to four neighboring atoms by four covalent bonds. In order for the covalent bonds to be formed, the silicon atoms must be arranged so the bonds have a fixed directional relationship with one another. Solids with covalent bonding generally possess high hardness and low electrical conductivity.

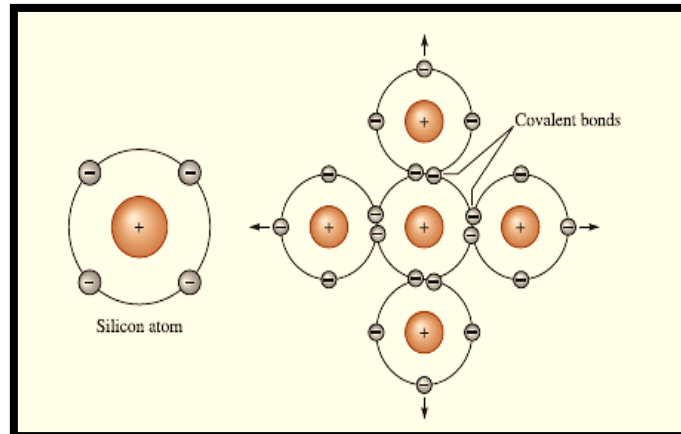


Figure 2. Covalent bonding requires that electrons be shared between atoms in such a way that each atom has its outer **sp** orbital filled. In silicon, with a valence of four, four covalent bonds must be formed for every atom.

3.The Ionic Bond: In the ionic bond, when more than one type of atoms are present in a material, one atom may donate its valence electrons to a different atom, filling the outer energy shell of the second atom. Both atoms now have filled (or emptied) outer energy levels, but both have acquired an electrical charge and behave as ions. The atom that contributes the electrons is left with a net positive charge and is called a **cation**, while the atom that accepts the electrons acquires a net negative charge and is called an **anion**. The oppositely charged ions are then attracted to one another and produce the **ionic bond**. This bond is naturally provides a very strong bond between atoms and as a properties of solid materials with the ionic bonding include low electrical conductivity and poor ductility.

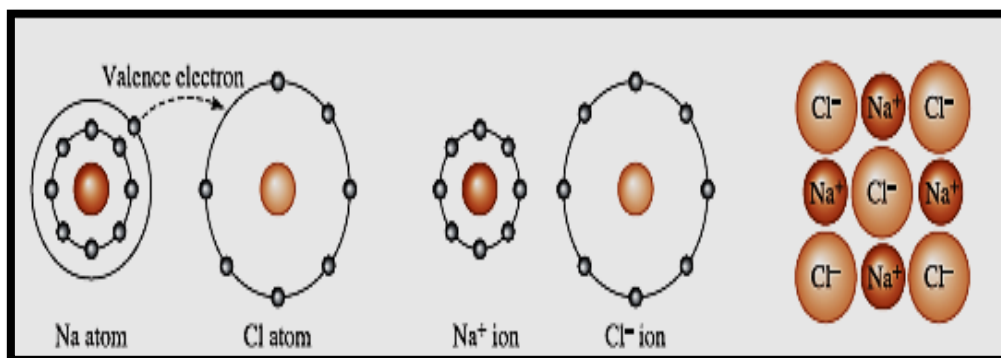


Figure 3. An ionic bond is created between two unlike atoms with different electronegativities. When sodium donates its valence electron to chlorine, each atom becomes an ion, and the ionic bond is formed.

Solids that exhibit considerable ionic bonding are also often mechanically strong because of the strength of the bonds. Electrical conductivity of ionically bonded solids is very limited. A large fraction of the electrical current is transferred via the movement of ions. Owing to their size, ions typically do not move as easily as electrons. However, in many technological applications we make use of the electrical conduction that can occur via movement of ions as a result of increased temperature, chemical potential gradient, or an electrochemical driving force. Examples of these include lithium ion batteries that make use of lithium cobalt oxide, conductive indium tin oxide (**ITO**) coatings on glass for touch sensitive displays, and solid oxide fuel cells (**SOFC**) based on compositions based on zirconia (**ZrO₂**).



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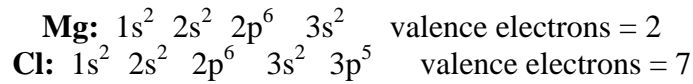


EXAMPLE.1 Describing the Ionic Bond Between Magnesium and Chlorine.

Describe the ionic bonding between magnesium and chlorine ???

SOLUTION

The electronic structures and valences are



Each magnesium atom gives up its two valence electrons, becoming a Mg^{+2} ion. Each chlorine atom accepts one electron, becoming a Cl^- ion. To achieve the ionic bonding, there must be twice as many chloride ions as magnesium ions present, and a compound, MgCl_2 , is formed.

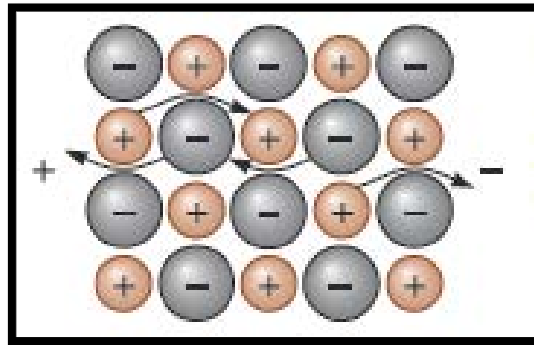


Figure 4. When voltage is applied to an ionic material, entire ions must move to cause a current to flow. Ion movement is slow and the electrical conductivity is poor at low temperatures (for Example 1).

4. Van der Waals Bonding: They are very small forces of attraction acting between atoms in cases where the formation of ionic or covalent bonds is not possible. Basically similar forces also act between atoms which are already bounded in neighboring molecules, giving rise to weak Van der Waal's forces between long-chain molecules in polymers.

Mixed Bonding: In most materials, bonding between atoms is a mixture of two or more types. **Iron**, for example, is bonded by a combination of metallic and covalent bonding that prevents atoms from packing as efficiently as we might expect.

Compounds formed from two or more metals (intermetallic compounds) may be bonded by a mixture of metallic and ionic bonds, particularly when there is a large difference in electronegativity between the elements. Because **lithium** has an electronegativity of **1.0** and **aluminum** has an electronegativity of **1.5**, we would expect **Al-Li** to have a combination of metallic and ionic bonding. On the other hand, because both **aluminum** and **vanadium** have electronegativity of **1.5**, we would expect **Al₃V** to be bonded primarily by metallic bonds.

Many **ceramic** and **semiconducting compounds**, which are combinations of metallic and nonmetallic elements, have a mixture of covalent and ionic bonding. As the electronegativity difference between the atoms increases, the bonding becomes more ionic. The fraction of bonding that is covalent can be estimated from the following equation:

$$\text{Fraction covalent} = \exp(-0.25 \Delta E^2)$$

Where

ΔE is the difference in electronegativity.