Crystallography and Atomic Bonding

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Nomenclature

a  lattice constant  m
r  radius  m

CRYSTALLOGRAPHY

Common Metallic Crystalline Structures

The energy of a stable aggregation of atoms in a compound is lower than the energy of the individual atoms, and therefore, the aggregation is the more stable configuration. The atoms configure themselves spontaneously in this stable configuration, without requiring external energy.

Common table salt, NaCl, is a stable crystalline solid. The formation of table salt from positive sodium and negative chlorine ions proceeds spontaneously upon mixture. The ions form a three-dimensional cubic lattice of alternating sodium and chlorine ions. Each ion of one charge has six neighbors of the opposite charge. The strong electrostatic attraction of these six neighbors provides the force that causes the crystal to form.

If the ions were merely positive and negative point charges, the arrangement of charges would collapse into itself. However, the inner electron shells of both positive and negative ions provide the repulsive force to keep the ions apart. At the equilibrium position, this repulsion just balances the ionic attraction.

There are 14 different three-dimensional crystalline structures, known as Bravais lattices, as illustrated in Fig. 40.1. The smallest repeating unit of a Bravais lattice is known as a cell or unit cell.

Figure 40.1 Crystalline Lattice Structures

The 14 basic point-lattices are illustrated by a unit cell of each: (1) simple triclinic, (2) simple monoclinic, (3) base-centered monoclinic, (4) simple orthorhombic, (5) base-centered orthorhombic, (6) body-centered orthorhombic, (7) face-centered orthorhombic, (8) hexagonal, (9) rhombohedral, (10) simple tetragonal, (11) body-centered tetragonal, (12) simple cubic, (13) body-centered cubic, and (14) face-centered cubic.
There are seven different basic cell systems: the cubic, tetragonal, orthorhombic, monoclinic, triclinic, hexagonal, and rhombohedral. Characteristics of these systems are listed in Table 40.1.

<table>
<thead>
<tr>
<th>system</th>
<th>sides</th>
<th>axial angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>cubic</td>
<td>$a_1 = a_2 = a_3$</td>
<td>all angles = 90°</td>
</tr>
<tr>
<td>tetragonal</td>
<td>$a_1 = a_2 = c$</td>
<td>all angles = 90°</td>
</tr>
<tr>
<td>orthorhombic</td>
<td>$a = b = c$</td>
<td>all angles = 90°</td>
</tr>
<tr>
<td>monoclinic</td>
<td>$a \neq b = c$</td>
<td>two angles = 90°;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>one angle $\neq 90°$</td>
</tr>
<tr>
<td>triclinic</td>
<td>$a \neq b \neq c$</td>
<td>all angles different;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>none equals 90°</td>
</tr>
<tr>
<td>hexagonal</td>
<td>$a_1 = a_2 = a_3$</td>
<td>angles = 90° and 120°</td>
</tr>
<tr>
<td>rhombohedral</td>
<td>$a_1 = a_2 = a_3$</td>
<td>all angles equal,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>but not 90°</td>
</tr>
</tbody>
</table>

Most common metallic crystals form in one of three cell systems: the body-centered cubic (BCC) cell, the face-centered cubic (FCC) cell, and the hexagonal close-packed (HCP) cell. Also, some of the simpler ceramic compounds (e.g., MgO, TiC, and BaTiO₃) are cubic. Table 40.2 lists common materials and their crystalline forms.

**Number of Atoms in a Cell**

When studying crystalline lattices, it is convenient to assume that the atoms have definite sizes and can be represented by hard spheres of radius $r$. The cell size, then, depends on the lattice type and the sizes of the touching spheres. On the basis of this representation, Fig. 40.2 illustrates three types of cubic structures and gives formulas for the center-to-center distances between the lattice atoms. The distances $a$, $b$, and $c$ are known as lattice constants.

Some of the atoms in a unit cell are completely contained within the cell boundary (e.g., the center atom in a BCC structure). Other atoms are shared by adjacent cells (e.g., the corner atoms). Because of this sharing, the number of atoms attributable to a cell is not the number of whole atoms appearing in the lattice structures shown in Fig. 40.1. For example, there are nine atoms shown for the BCC structure. Although the center atom is completely enclosed, each of the eight corner atoms is shared by eight cells. Therefore, the number of atoms (also known as the number of lattice points) in a cell is $1 + (1/8)(8) = 2$.

**Packing Factor**

The packing factor is the volume of the atoms divided by the cell volume (i.e., $a^3$ for a cubic structure). These parameters are summarized in Table 40.3 for hard touching spheres of radius $r$.

The low packing factor of the simple cubic and simple hexagonal structure indicates that these cells are wasteful of space. This is the primary reason simple cubic and hexagonal lattices seldom form naturally.
Figure 40.2(b) Cubic Lattice Dimensions Body-Centered Cubic

<table>
<thead>
<tr>
<th>distance between atoms</th>
<th>in terms of ( r )</th>
<th>in terms of ( a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 and 2</td>
<td>( \frac{4r}{\sqrt{3}} )</td>
<td>( a )</td>
</tr>
<tr>
<td>1 and 4</td>
<td>( 4r \sqrt{\frac{2}{3}} )</td>
<td>( \sqrt{2}a )</td>
</tr>
<tr>
<td>1 and 9</td>
<td>( 2r \left( \frac{\sqrt{3}}{2} \right) )</td>
<td>( a )</td>
</tr>
<tr>
<td>1 and 8</td>
<td>( 4r )</td>
<td>( \sqrt{3}a )</td>
</tr>
</tbody>
</table>

Figure 40.3 Cell Packing Parameters (assuming hard touching spheres)

<table>
<thead>
<tr>
<th>type of cell</th>
<th>number of atoms in a cell</th>
<th>packing factor</th>
<th>coordination number</th>
</tr>
</thead>
<tbody>
<tr>
<td>simple cubic</td>
<td>1</td>
<td>0.52</td>
<td>6</td>
</tr>
<tr>
<td>body-centered cubic</td>
<td>2</td>
<td>0.68</td>
<td>8</td>
</tr>
<tr>
<td>face-centered cubic</td>
<td>4</td>
<td>0.74</td>
<td>12</td>
</tr>
<tr>
<td>simple hexagonal</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>primitive cell</td>
<td>1</td>
<td>0.52</td>
<td>8</td>
</tr>
<tr>
<td>total structure</td>
<td>3</td>
<td>0.52</td>
<td>8</td>
</tr>
<tr>
<td>hexagonal close-packed</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>primitive cell</td>
<td>2</td>
<td>0.74</td>
<td>12</td>
</tr>
<tr>
<td>total structure</td>
<td>6</td>
<td>0.74</td>
<td>12</td>
</tr>
</tbody>
</table>

**Coordination Number**

The coordination number of an atom in an ionic compound is the number of closest (touching) atoms. Since the atoms in an ionic solid are actually ions, another definition of coordination number is the number of anions surrounding each cation.

In reality, ions in a crystal are not all the same radius. The size of a cation that can fit in a site (known as interstices or interstitial spaces) between the anions is a function of the relative sizes of the ions.

**Miller Indices**

Crystallography uses a system known as Miller indices to specify planes in crystalline lattices. Planes are designated by numbers enclosed in parentheses, one for each coordinate direction in the unit cell.

Consider an orthorhombic cell that has cell dimensions \( a \), \( b \), and \( c \) in the \( x \)-, \( y \)-, and \( z \)-axes. The Miller indices are calculated as the reciprocals of the plane intercepts on these axes. If the plane does not intersect a cell axis, the intercept is infinity. By convention, there are no fractional intercepts, so the indices are multiplied by the least common denominator to clear all fractions. They are reduced to the smallest integers and written without commas, with overbars used to designate negative numbers.

For example, \((0 \overline{1} \overline{1})\) indicates a plane that intersects the \( x \)-axis at infinity (i.e., it does not intersect), the \( y \)-axis at a unit distance \( b \) from the origin, and the \( z \)-axis at a unit distance \( c \) from the origin (Fig. 40.3(a)). \((2 \overline{1} \overline{1})\) indicates a plane that intersects the \( x \)-axis at a distance of \( a/2 \), the \( y \)-axis at a distance \(-b \), and the \( z \)-axis at a distance \( c \) from the origin (Fig. 40.3(b)).

Due to the symmetry of cubic systems, there are many crystallographically equivalent planes. Families of equivalent planes are written as \( \{hkl\} \). For example, the
ATOMIC BONDING

There are three types of primary bonds between atoms in molecular structures: ionic, covalent, and metallic. Intermolecular bonds, known as Van der Waals forces, also exist. These are called secondary bonds because they are much weaker than the primary bonds.

Anions and cations are attracted to each other by electrostatic force. The electrostatic attraction of the positive cation to the negative anion effectively binds the two ions together. This type of bonding, in which electrostatic attraction is predominant, is known as ionic bonding. One or more electrons are transferred from the valence shell of one atom to the valence shell of another. There is no sharing of electrons between atoms. Ionic bonding is characteristic of compounds of atoms with high electron affinities and atoms with low ionization energies (e.g., salts or metal oxides). The difference in electronegativities must be approximately 1.7 or greater for the bond to be classified as ionic.

Several common gases in their free states exist as diatomic molecules. Examples are hydrogen (H₂), oxygen (O₂), nitrogen (N₂), and chlorine (Cl₂). Since two atoms of the same element will have the same electronegativity and ionization energy, it is unlikely that one atom will take electrons from the other. Therefore, the bond formed is not ionic. Bonding in which the sharing of electrons is the predominant characteristic is known as covalent bonding. Covalent bonds are typical of bonds formed in organic and polymer compounds.

If the atoms are both the same element, the electrons will be shared equally and the bond will be purely covalent; but if the atoms are not both the same element, the electrons will not be shared equally and the bond will be partially covalent and partially ionic in nature. There is no sharp dividing line between ionic and covalent bonds for most compounds; if the difference in electronegativities is less than approximately 1.7, then the bond is classified as covalent.

Metallic bonding occurs when atoms contain electrons that are free to move from atom to atom. The sea of electrons is attracted to the positive ions in the metal structure, and this attraction bonds the atoms. Such bonding is nondirectional, as the electrons typically can move in three dimensions.
SAMPLE PROBLEMS

Problem 1
Which of the following elements does not have a face-centered cubic structure?

(A) aluminum
(B) copper
(C) silver
(D) sodium

Solution
Each of the materials except sodium has a face-centered cubic structure. Sodium has a body-centered cubic structure, but note that sodium chloride, NaCl, has a face-centered cubic structure.

Answer is D.

Problem 2
How many atoms are in the simple hexagonal structure shown?

(A) 1
(B) 2
(C) 3
(D) 6

Solution
This is a simple hexagonal unit cell, not a hexagonal close-packed cell. The two center end atoms are each shared by two unit cells. The corner atoms are each shared by six unit cells.

\[
\frac{\text{no. of atoms}}{\text{unit cell}} = \frac{2 \text{ atoms}}{2 \text{ cells}} + \frac{12 \text{ atoms}}{6 \text{ cells}} = \frac{1}{1} + \frac{2}{2} = 3
\]

Note that there are three primitive cells within the simple hexagonal structure. There is one atom in each primitive cell.

Answer is C.

Problem 3
What are the Miller indices of the plane shown?

(A) (1 \(\frac{1}{2}\) 0)
(B) (2 1 0)
(C) (1 2 0)
(D) (1 2 \(\infty\))

Solution
The intercepts along the \(x\)-, \(y\)-, and \(z\)-axes are 1, 1/2, and \(\infty\). The reciprocals are \(h = 1\), \(k = 2\), and \(l = 0\). The Miller indices are (1 2 0).

Answer is C.

FE-STYLE EXAM PROBLEMS

1. What is the packing factor for the unit cell shown?

(A) 0.35
(B) 0.50
(C) 0.52
(D) 0.68

2. What is the coordination number of a face-centered cubic unit cell?

(A) 6
(B) 8
(C) 10
(D) 12
3. What are the Miller indices of the plane shown?

(A) (1 2 1)
(B) (0 2 1)
(C) (1 1/2 1)
(D) (0 1/2 1)

4. Which of the following planes is a member of the \{1 1 0\} family?

(A) (1 0 0)
(B) (1 0 1)
(C) (1 1 1)
(D) (0 0 1)

5. What type is the crystalline structure shown?

(A) simple cubic
(B) body-centered cubic
(C) face-centered cubic
(D) hexagonal close-packed

For the following problems use the NCEES Handbook as your only reference.

6. How many atoms are in a hexagonal close-packed cell?

(A) 2
(B) 4
(C) 6
(D) 8

7. Which of the following is the strongest type of bond?

(A) Van der Waals
(B) ionic
(C) covalent
(D) metallic

8. Which metals form crystals in a hexagonal close-packed structure?

I. magnesium
II. zinc
III. titanium
IV. iron

(A) I only
(B) I and II
(C) I and III
(D) I, II, and III

SOLUTIONS TO FE-STYLE EXAM PROBLEMS

1. The unit cell has a simple cubic structure. The packing factor is the volume of the atoms divided by the cell volume. In a simple cubic structure there is one atom per cell unit (each of the eight atoms shown shares with eight other unit cells). Assuming hard touching spheres of radius \(r\), the length of the unit cell \(a = 2r\).

\[
\text{packing factor} = \frac{(1 \text{ atom})}{a^3} \left(\frac{4\pi r^3}{3}\right)
\]

\[
= \frac{4\pi r^3}{(3)(2r)^3}
\]

\[
= \frac{4\pi}{(3)(8)}
\]

\[
= 0.52
\]

Answer is C.

2. Each face-centered atom has 12 closest neighbors, as the following illustration shows.

Answer is D.

3. This is a tricky question because the cell used to obtain the intercepts is not shown. Use the cell immediately behind the left-most cell shown.

The intercepts along the \(x\), \(y\), and \(z\)-axes are \(-1\), \(1/2\), and \(1\). The reciprocals are \(h = -1\), \(k = 2\), and \(l = 1\). The Miller indices are written \((\overline{1} 2 1)\).

Answer is A.
4. Due to the symmetry of a cubic structure, the choice of origin in a unit cell may be arbitrary, and thus, families of planes contain planes that are equivalent.

The plane (1 0 1) is equivalent to plane (1 1 0) and therefore, is in the same family. Verify this result by sketching the plane of the correct answer choice, and some of the incorrect answer choices, on a unit cell.

Answer is B.

5. The crystalline structure shown is the common body-centered cubic.

Answer is B.

6.

Each of the twelve edge atoms is shared by six cells (three in each layer). The two center atoms in the ends are shared by two complete cells (one in each layer). There are also three enclosed atoms.

\[
\text{no. of atoms} = \frac{12}{6} + \frac{2}{2} + 3 = 6
\]

Answer is C.

7. Covalent bonding is much stronger than ionic bonding (which is essentially electrostatic in nature). Electrons are easily displaced in metals by small voltages. Van der Waals forces in gases are so small as to be essentially negligible at normal temperatures.

Answer is C.

8. Hexagonal close-packed is the crystalline structure for magnesium, titanium, and zinc. Alpha- and delta-iron have a BCC structure, and gamma-iron has an FCC structure.

Answer is D.