

3.091 – Introduction to Solid State Chemistry

Lecture Notes No. 4

THE NATURE OF CRYSTALLINE SOLIDS

In an assembly of atoms or molecules a solid phase is formed whenever the interatomic (intermolecular) attractive forces significantly exceed the disruptive thermal forces and thus restrict the mobility of atoms, forcing them into more-or-less fixed positions. From energy considerations it is evident (as discussed in LN-2) that in such solids the atoms or molecules will always attempt to assume highly ordered structures which are characterized by *symmetry*. Depending on the nature of the acting interatomic forces, all solids may be subdivided into:

- | | | |
|-----|----------------------|-----------------|
| (a) | Ionic solids | (NaCl) |
| (b) | Covalent solids | (Diamond) |
| (c) | Metallic solids | (Fe, Ni, etc.) |
| (d) | Van der Waals solids | (ice, solid He) |

Solids as we encounter them in nature may or may not reflect the internally ordered arrangement in their appearance. We find, for example, well-formed quartz crystals, garnets, diamonds and snowflakes which are all characterized by flat bounding planes which intersect at characteristic angles. On the other hand, we also observe rounded stones and man-made cast solid objects with no external evidence of internal order

(fig. 1).

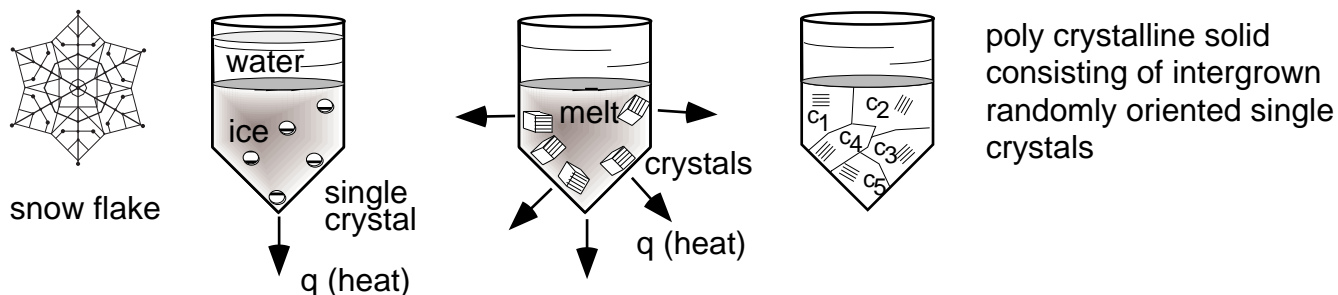


Figure 1 Crystals, internal order and external appearance

To understand the external appearance of the solid state it is necessary to consider the formation of solids from different *phases*. Solids, for example, are formed upon cooling of liquids (melts) - by freezing or solidification; this solidification process normally proceeds in total confinement and the resulting “cast” structure will have an external appearance which reflects in detail the confining geometry (and not the internal order). Moreover, depending on solidification conditions, the solid body may be either a *single crystal* or *polycrystalline*. Polycrystalline solids (in excess of 95% of the solid state encountered) may be thought of as an assembly of microscopic single crystals with random orientation held together like a maze structure by the interwoven irregular shapes of the individual crystals.

A typical example of an “unconfined” phase transformation is the formation of snowflakes where the external boundaries of the solid have assumed *crystalline* appearance, reflecting in detail the internally ordered molecular (H_2O) arrangement. Another unconfined formation of a solid is precipitation from solution (sugar crystals, $CuSO_4$ and the like). Similarly, the formation of crystals from the vapor phase leads to bodies which externally reflect elements of internal order.

1. CRYSTAL STRUCTURE

From the earlier discussion it should be apparent that, when strong interatomic forces exist, atoms tend to pack closely together - the closeness of packing being particularly pronounced in the solid state. In this case atoms can be regarded as hard spheres and the problem of close packing can be treated as one in which the whole assembly has a tendency toward efficient packing. A little thought or a few simple experiments with ping-pong balls quickly convince us that regular arrangements of the spheres generally lead to more compact assemblies than irregular arrangements (fig. 2). The same principle applies to arrangement of atoms in the solid state. Where strong attractive forces are exerted we find that the atoms or molecules concerned arrange themselves

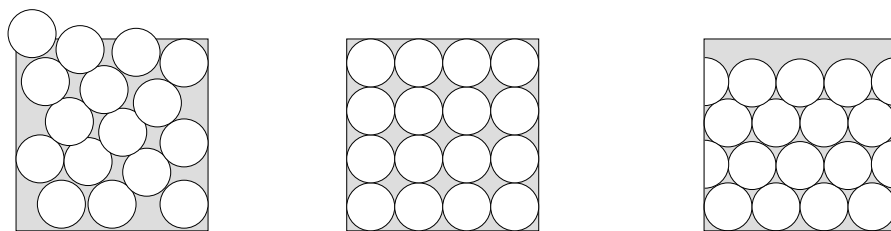


Figure 2 The packing density of ordered systems.

in a regular three-dimensional pattern. It is this regularity which is the basis of crystallinity in materials: i.e., *a crystal structure is nothing more than an orderly array of atoms or molecules*. This definition of a crystal is distinct from the popular concept based on observation of external symmetry of crystals, often seen during the study of elementary chemistry, in which some crystals appear cubic, others needle-shaped and so on. The regular external shape is obtained only when the conditions of crystallization are favorable to development of flat, geometric faces. In most instances, particularly with metals, these conditions are absent, and the crystals have irregular surfaces even though the internal arrangement is perfectly geometric.

Atomic arrays in crystals are conveniently described with respect to a three-dimensional net of straight lines. Consider a lattice of lines, as in fig. 3, dividing space into equal-sized prisms which stand side-by-side with all faces in contact, thereby filling all space and leaving no voids. The intersections of these lines are points of a *space lattice*, i.e., *a geometrical abstraction* which is useful as a reference in describing and correlating symmetry of actual crystals. These lattice points are of fundamental importance in describing crystals for they may be the positions occupied by individual atoms in crystals or they may be points about which several atoms are clustered. Since prisms of many different shapes can be drawn through the points of a space lattice to partition it into cells, the manner in which the network of reference lines is drawn is arbitrary. It is not necessary that the lines be drawn so that atoms lie only at corners of unit prisms. In fact, it is more convenient to describe some crystals with respect to

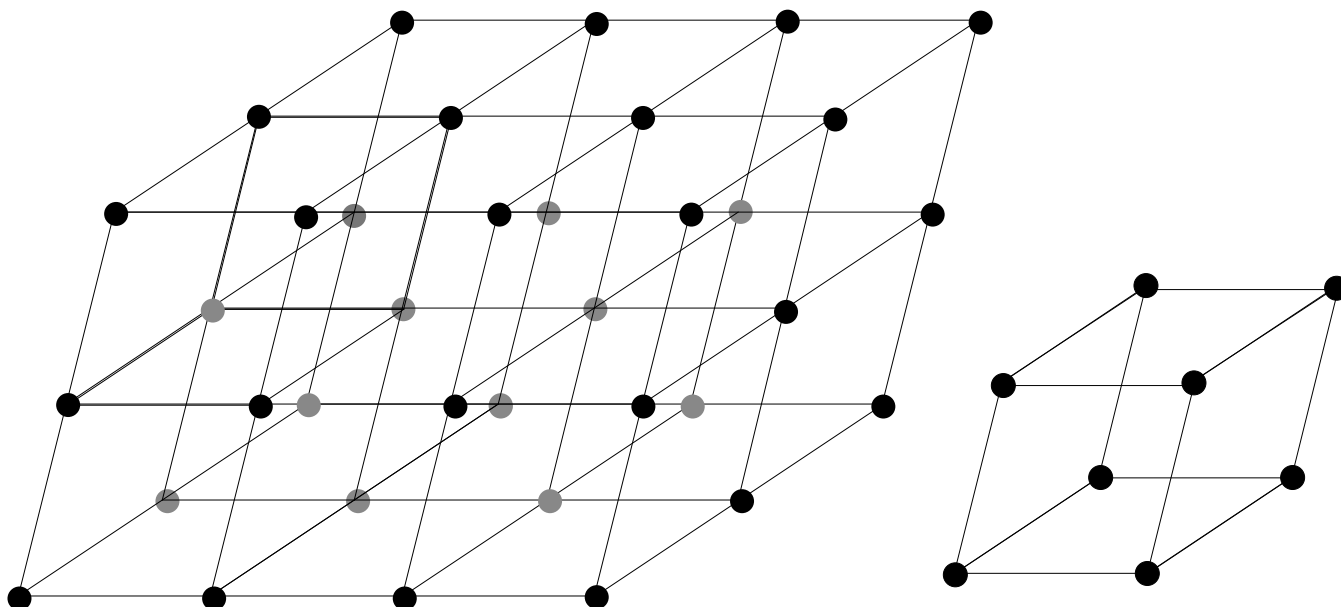


Figure 3 The space lattice prisms in which atoms lie at prism centers or at the centers of prism faces as well as at prism corners.

An important characteristic of a space lattice is that every point has identical surroundings: the grouping of lattice points about any given point is identical to the grouping about any other point in the lattice. In other words, if we could move about in the lattice, we would not be able to distinguish one point from another because rows and planes near each point would be identical. If we were to wander among the atoms of a solid metal or chemical compound, we would find the view from any lattice point exactly the same as that from any other.

There are fourteen space lattices (fig. 4). That is, no more than fourteen ways can be found in which points can be arranged in space so that each point has identical surroundings. Of course, there are many more than fourteen ways in which atoms can be arranged in actual crystals; thus there are a great number of crystal *structures*. Too often the term “lattice” is loosely used as a synonym for “structure”, an incorrect practice which is frequently confusing. The distinction can be clearly seen if we

7 Crystal systems

14 Bravais Lattices

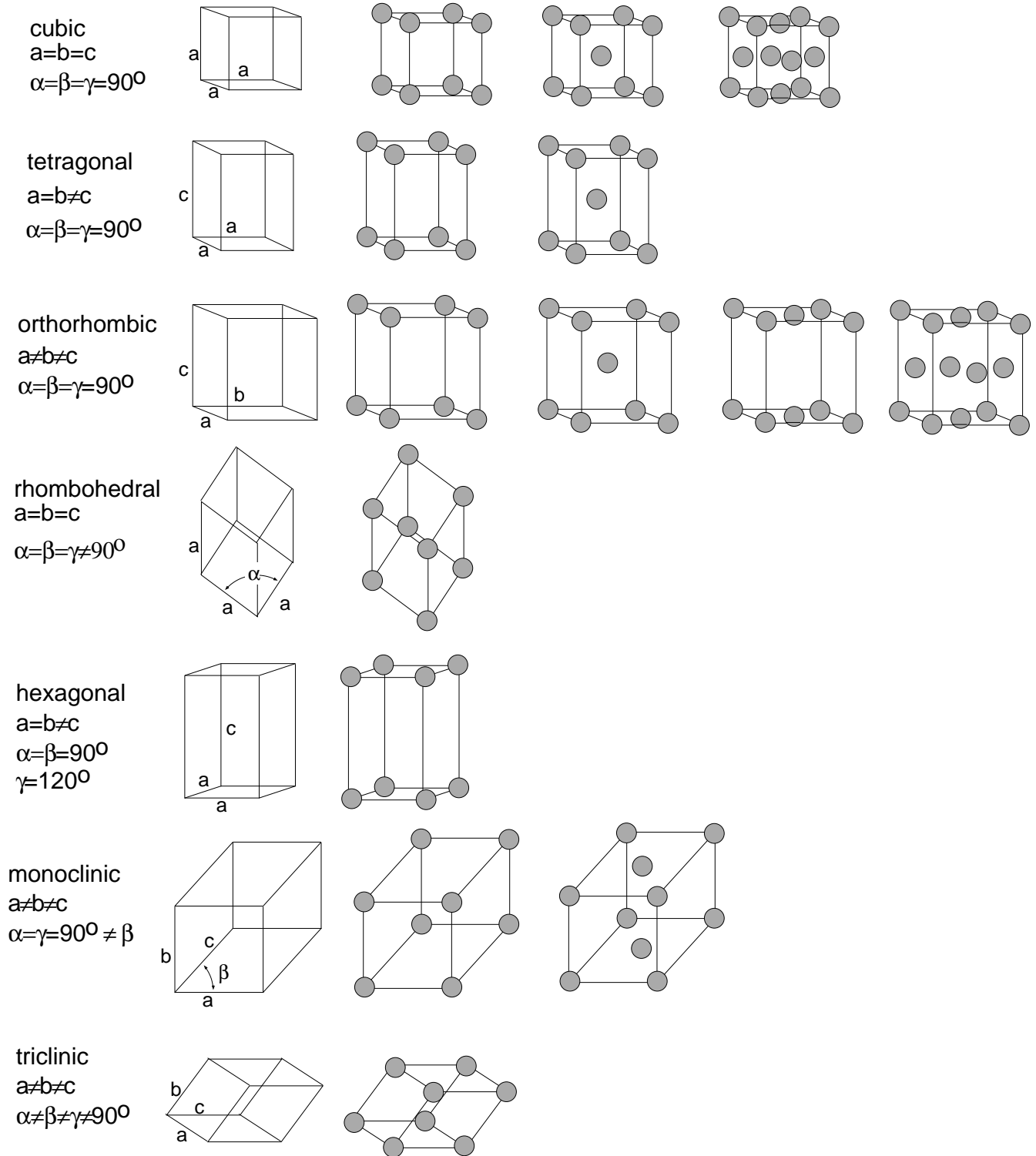


Figure 4 The 7 crystal systems and the 14 Bravais lattices

remember that a space lattice is an array of points in space. It is a geometrical abstraction which is useful only as a reference in describing and correlating symmetry of actual crystals. A crystal structure, however, is the arrangement of atoms or molecules which actually exists in a crystal. It is a dynamic, rather than a static, arrangement and is subject to many imperfections. Although any crystal structure has an inherent symmetry which corresponds to one of the fourteen space lattices, one, two or several atoms or molecules in the crystal structure may be associated with each point of the space lattice. This symmetry can be maintained with an infinite number of different actual arrangements of atoms - making possible an endless number of crystal structures.

To specify a given arrangement of points in a space lattice, it is customary to identify a unit cell with a set of coordinate axes, chosen to have an origin at one of the lattice points (fig. 5). In a cubic lattice, for example, we choose three axes of equal length that

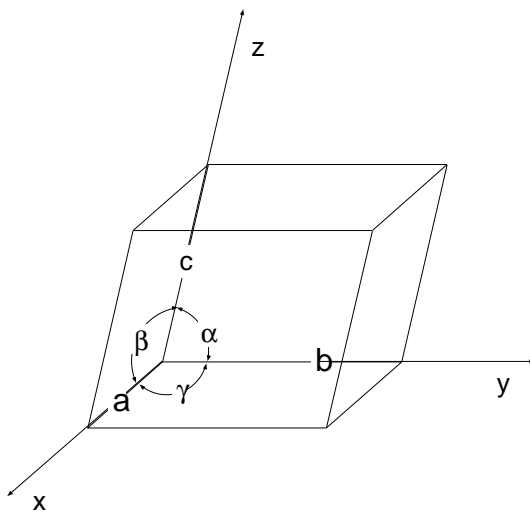


Figure 5 Specification of Unit Cell parameters

are mutually perpendicular and form three edges of a cube. Each space lattice has some convenient set of axes, but they are not necessarily equal in length or orthogonal. Seven different systems of axes are used in crystallography, each possessing certain

characteristics as to equality of angles and equality of lengths. These seven crystal systems are tabulated in Table I (to be considered in conjunction with fig. 4).

Table I. The Seven Crystal Systems

System	Parameters	Interaxial Angles
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma$
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ \neq \beta$
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma$
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma$
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$

The network of lines through the points of a space lattice (fig. 3) divides it into *unit cells* (see also fig. 4). Each unit cell in a space lattice is identical in size, shape and orientation to every other unit cell. It is the building block from which the crystal is constructed by repetition in three dimensions. The unit cells of the fourteen space lattices are shown in fig. 4. All crystal structures are based on these fourteen arrangements.

The body-centered cubic, face-centered cubic and hexagonal lattices are common and of prime importance in metals. Some of the metals associated with nuclear applications, such as uranium and plutonium, have crystal structures which are more complicated

than these three relatively simple types. In general, crystalline ceramics also are more complex.

2. UNIT CELLS VS PRIMITIVE CELLS

In the literature we often find reference to unit cells and to primitive cells. The primitive cell may be defined as a geometrical shape which, when repeated indefinitely in three dimensions, will fill all space and is the equivalent of one atom. The unit cell differs from the primitive cell in that it is not restricted to being the equivalent of one atom. In some cases the two coincide. For instance, in fig. 4 all fourteen space lattices are shown by their unit cells. Of these fourteen, only seven (which are those?) are also primitive cells.

Primitive cells are drawn with lattice points at all corners, and each primitive cell contains the equivalent of one atom. For instance, a simple cubic unit cell has an atom at each corner. However, at any of these given corners, this atom must be shared with seven other identical cubes which fill the volume surrounding this point. Thus there is effectively only $1/8$ of the atom which can be assigned to that particular unit cell. Since there are eight corners in a cube, there is the equivalent of one atom, and thus the primitive cell and unit cell coincide.

Continuing, consider the *body-centered cubic* (BCC) lattice. In this case there is one atom at the center of the cube and one atom contributed by the eight corners. This cell, then, has two atoms and, to avoid confusion, should be termed a unit cell. In the *face-centered cubic* lattice there are six face atoms, but each face atom is shared by two cells. Consequently, each face contributes $1/2$ an atom. The faces thus contribute three atoms and the corners one, for a total of four atoms in the unit cell. The face-centered cubic structure (FCC) can also be considered as four interpenetrating simple cubic cells.

In the study of crystals the primitive cell has limited use because the unit cell more clearly demonstrates the symmetrical features of a lattice. In other words, the unit cell can usually be visualized readily whereas the primitive cell cannot. For example, the cubic nature of the face-centered cubic lattice is immediately apparent in the unit cell, but it is not nearly so obvious in the rhombohedral primitive cell.

3. PACKING OF ATOMS

A crystal structure is a regular array of atoms arranged on one of the fourteen space lattices. The least complicated crystal structures are those having a single atom at each lattice point. Polonium has the simplest structure, being simple cubic. In normal metals, the atoms (or positive ions) are held together by a cloud of free electrons so that each atom tends to be attracted equally and indiscriminately to all its geometrically nearest neighbors by the free electrons passing between them. This condition fosters the formation of closely packed structures of the types which can be demonstrated by efficiently packing uniformly-sized spheres into a given volume.

You can gain a better grasp of packing by conducting an experiment as follows. Assume we have a quantity of small spheres which we are required to efficiently pack into a box (a 'two-dimensional' approach can be made using a handful of pennies). After some shuffling, it is obvious that the closest possible packing is obtained when the spheres are in contact and their centers occupy positions which correspond to the apices of equilateral triangles (fig. 6). It is also evident that there are two sets of

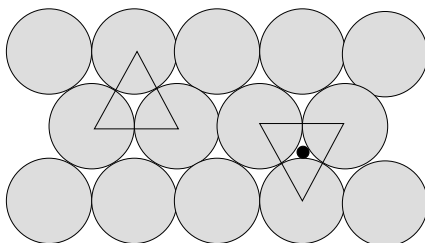


Figure 6 Close packed atomic arrangements

triangles – one set with vertices pointing away from the observer (points up) and the other set with vertices pointing toward the observer (points down).

When a second layer is added, there is closest-packing if the spheres in this new layer rest in the hollows formed by the spheres of the first layer. The centers of the spheres in the second layer will lie above the centers of the points-up triangles or above the centers of the points-down triangles, but not both simultaneously. Which set is used is immaterial. For our discussion, however, assume the second layer is centered on the points-up triangles.

When we start adding a third layer, the spheres will again rest in the hollows formed by the spheres in the second layer. And again we have the option of placing the third layer on the points-up or on the points-down triangles. If we center the third layer on the points-down triangles, we find the third layer is directly above the first layer. If additional layers are added using an alternate stacking sequence (i.e., alternately centering the layers on the points-up and the points-down triangles), the sequence can be written as ABABABAB. . . This arrangement of spheres, translated to an arrangement of atoms, is the hexagonal close-packed (HCP) structure - very important, but not discussed in detail here.

Many elements having covalent bonding form arrangements in which the coordination number is $(8-N)$, where N is the number of valence electrons. What, then, is the coordination number of the HCP structure just demonstrated? The geometry of the structure shows that any one atom has twelve equidistant neighbors. It is apparent that if, in any layer, a given sphere is placed in the adjoining layer, it fits in the hollow formed by three spheres and consequently is tangent to three spheres in the adjoining layer. Thus any given atom in the HCP structure is tangent to twelve other atoms – six in its own layer and three each in two adjoining layers.

When the third layer of spheres was added in the above discussion, we assumed this layer was centered on the points-down triangles of the second layer. What happens if the centers of the points-up triangles of the second layer are used instead? The distribution of spheres in the third layer is the same as in the first two layers, but does not lie directly above either of these two layers. If a fourth layer is added, centered on the points-up triangles of the third layer, we find the fourth layer is directly above the first layer and duplicates it completely. The stacking sequence for this structure can be written as ABCABCABC. . . This arrangement has the same density of packing and the same coordination number as the HCP structure. However, it is the face-centered cubic (FCC) structure.

The HCP and FCC crystal structures have the same density of packing and the same coordination number. Therefore we might expect the behavior of the two HCP and FCC structures to be very much alike with regard to physical and mechanical properties. This, however, in most instances is not the case.

The maximum density of packing is found only in the HCP and FCC crystal structures. Why the metallic bond does not always produce one or the other of these two densest arrangements of atoms is as yet subject of intensive studies. The BCC unit cell contains two atoms, and the coordination number is eight. There is partial compensation for this in the fact that there are six next-nearest neighbors at distances only slightly greater than that of the eight nearest neighbors. Some characteristics of cubic structures are given in Table II.

An interesting example of the type of crystal structure obtained in covalently bonded elements which obey the $(8-N)$ coordination number rule (where N is the number of valence electrons) is the diamond structure. This structure is found in carbon, germanium, silicon, and tin at low temperatures and in certain compounds. Each atom

has four nearest neighbors – a configuration that is variously called diamond cubic, body-centered tetrahedral or tetrahedral cubic.

TABLE II. Characteristics of Cubic Lattices

	<u>Simple</u>	<u>Body-Centered</u>	<u>Face-Centered</u>
Unit Cell Volume	a^3	a^3	a^3
Lattice Points Per Cell	1	2	4
Nearest Neighbor Distance	a	$\frac{a\sqrt{3}}{2}$	$\frac{a}{\sqrt{2}}$
Number of Nearest Neighbors	6	8	12
Second Nearest Neighbor Distance	$a\sqrt{2}$	a	a
Number of Second Neighbors	12	6	6

Many compounds crystallize in variations of cubic forms. Rock salt (NaCl), for example, is typical of many oxides, fluorides, chlorides, hydrides and carbides. It is sometimes considered as simple cubic with alternate Na and Cl atoms on the cube corners.

Actually the structure is two interpenetrating FCC lattices – one of Na and the other of Cl – and the corner of one is located at point $1/2, 0, 0$ of the other.

Many other oxides, fluorides and some intermetallic compounds have the fluorite (CaF_2) structure. This is FCC with Ca at the cube corners and face centers and F at all quarter points along the cube diagonals.

4. LATTICE PLANES AND DIRECTIONS

It is desirable to have a system of notation for planes within a crystal or space lattice such that the system specifies orientation without giving position in space. *Miller indices* are used for this purpose. These indices are based on the intercepts of a plane with the three crystal axes – i.e., the three edges of the unit cell. The intercepts are measured in terms of the edge lengths or dimensions of the unit cell which are the unit distances from the origin along the three axes. For instance, the plane that cuts the x-axis at a distance from the origin equal to one-half the x-dimension of the cell is said to have an x-intercept equal to 1/2, and if it cuts the y-axis at 1/2 the y-dimension of the cell, the y-intercept is 1/2, regardless of the relative magnitudes of the x- and y-dimensions. If a plane is parallel to an axis, it intercepts the axis at infinity.

To determine Miller indices (hkl) of a plane, we take the following steps:

1. Find the intercepts on the three axes in multiples or fractions of the edge lengths along each axis.
2. Determine the reciprocals of these numbers.
3. Reduce the reciprocals to the three smallest integers having the same ratio as the reciprocals.
4. Enclose these three integral numbers in parentheses, e.g., (hkl).

A cube has six equivalent faces. If we have a definite orientation and wish to discuss one specific plane of these six, it is possible to specify this plane by using the proper Miller indices. Parentheses are used around the Miller indices to signify a specific plane. On the other hand, it is often advantageous to talk about planes of a “form” – i.e., a family of equivalent planes such as the six faces of a cube. To do this it is customary to use the Miller indices, but to enclose them in curly brackets (braces). Thus the set of cube faces can be represented as {100} in which

$$\{100\} = (100) + (010) + (001) + (\bar{1}00) + (0\bar{1}0) + (00\bar{1})$$

This notation thus provides a shorthand scheme to avoid writing the indices for all six cube faces.

The utility of the scheme is even more evident in the case of the (110) planes – i.e., the dodecahedral planes (in a cubic system), where

$$\begin{aligned} \{110\} = & (110) + (101) + (011) + (\bar{1}10) + (\bar{1}01) + (0\bar{1}1) \\ & + (1\bar{1}0) + (10\bar{1}) + (01\bar{1}) + (\bar{1}\bar{1}0) + (\bar{1}0\bar{1}) + (0\bar{1}\bar{1}) \end{aligned}$$

The equivalent form for the orthorhombic system is

$$\begin{aligned} \{110\} &= (110) + (\bar{1}10) + (1\bar{1}0) + (\bar{1}\bar{1}0) \\ \{101\} &= (101) + (\bar{1}01) + (10\bar{1}) + (\bar{1}0\bar{1}) \\ \{011\} &= (011) + (0\bar{1}1) + (01\bar{1}) + (0\bar{1}\bar{1}) \end{aligned}$$

The octahedral planes for the cube are

$$\begin{aligned} \{111\} = & (111) + (\bar{1}\bar{1}1) + (1\bar{1}\bar{1}) + (11\bar{1}) \\ & + (\bar{1}\bar{1}\bar{1}) + (\bar{1}1\bar{1}) + (1\bar{1}1) + (\bar{1}11) \end{aligned}$$

Direction indices are defined in a different manner. A line is constructed through the origin of the crystal axis in the direction under consideration and the coordinates of a point on the line are determined in multiples of lattice parameters of the unit cell. The indices of the direction are taken as the smallest integers proportional to these coordinates and are closed in square brackets. For example, suppose the coordinates are $x = 3a$, $y = b$ and $z = c/2$, then the smallest integers proportional to these three numbers are 6, 2 and 1 and the line has a [621] direction. As further examples, the x-axis has direction indices [100], the y-axis [010] and the z-axis [001]. A face diagonal of the xy face of the unit cell has direction indices [110], and a body diagonal of the cell has direction indices [111]. Negative indices occur if any of the coordinates are negative. For example, the -y axis has indices [0 $\bar{1}$ 0]. A full set of equivalent directions, i.e., directions of a form, are indicated by carets: <uvw>.

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