

Geometry of Crystals

2-1 INTRODUCTION

Turning from the properties of x-rays, we must now consider the geometry and structure of crystals in order to discover what there is about crystals in general that enables them to diffract x-rays. We must also consider particular crystals of various kinds and how the very large number of crystals found in nature are classified into a relatively small number of groups. Finally, we will examine the ways in which the orientation of lines and planes in crystals can be represented in terms of symbols or in graphical form.

Crystallography is a very broad subject. In this book we are concerned only with its simpler aspects: how atoms are arranged in some common crystals and how this arrangement determines the way in which a particular crystal diffracts x-rays. Readers who need a deeper knowledge of crystallography should consult such books as those by Phillips [G.38], Buerger [G.35], and Kelly and Groves [G.33].

2-2 LATTICES

A crystal may be defined as *a solid composed of atoms arranged in a pattern periodic in three dimensions*. As such, crystals differ in a fundamental way from gases and liquids because the atomic arrangements in the latter do not possess the essential requirement of periodicity. Not all solids are crystalline, however; some are *amorphous*, like glass, and do not have any regular interior arrangement of atoms. There is, in fact, no essential difference between an amorphous solid and a liquid, and the former is often referred to as an "undercooled liquid."

In thinking about crystals, it is often convenient to ignore the actual atoms composing the crystal and their periodic arrangement in space, and to think instead of a set of imaginary points which has a fixed relation in space to the atoms of the crystal and which may be regarded as a sort of framework or skeleton on which the actual crystal is built.

This set of points can be formed as follows. Imagine space to be divided by three sets of planes, the planes in each set being parallel and equally spaced. This division of space will produce a set of cells each identical in size, shape, and orientation to its neighbors. Each cell is a parallelepiped, since its opposite faces are parallel and each face is a parallelogram. The space-dividing planes will intersect each other in a set of lines (Fig. 2-1), and these lines in turn intersect in the

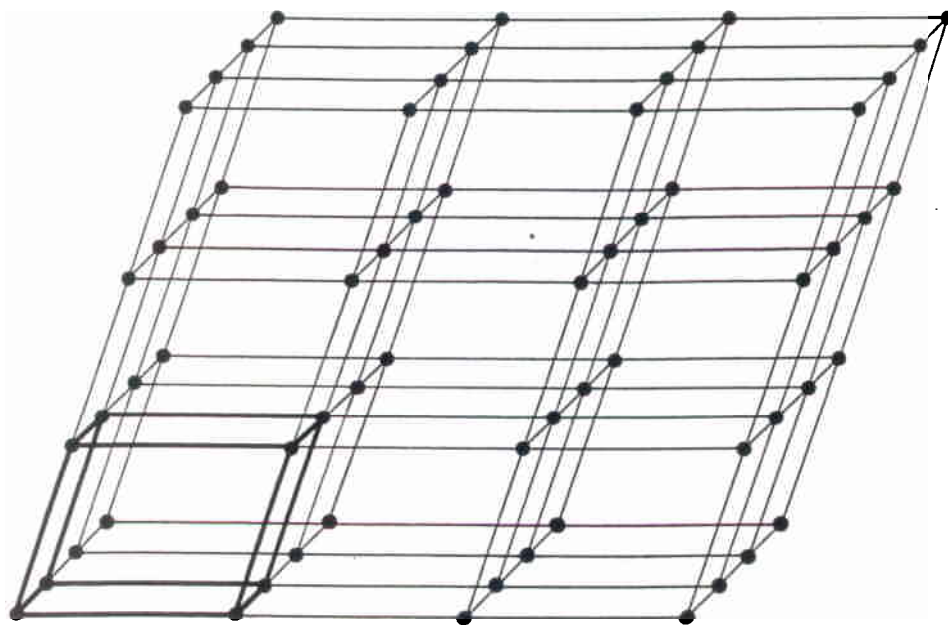


Fig. 2-1 A point lattice.

set of points referred to above. A set of points so formed has an important property: it constitutes a *point lattice*, which is defined as *an array of points in space so arranged that each point has identical surroundings*. By “identical surroundings” we mean that the lattice of points, when viewed in a particular direction from one lattice point, would have exactly the same appearance when viewed in the same direction from any other lattice point.

Since all the cells of the lattice shown in Fig. 2-1 are identical, we may choose any one, for example the heavily outlined one, as a *unit cell*. The size and shape of the unit cell can in turn be described by the three vectors* **a**, **b**, and **c** drawn from one corner of the cell taken as origin (Fig. 2-2). These vectors define the cell and are called the *crystallographic axes* of the cell. They may also be described in terms of their lengths (a , b , c) and the angles between them (α , β , γ). These lengths and angles are the *lattice constants* or *lattice parameters* of the unit cell.

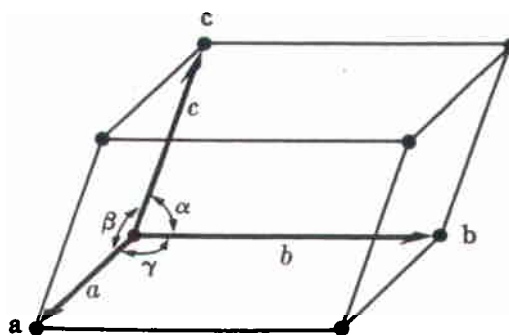


Fig. 2-2 A unit cell.

* Vectors are here represented by boldface symbols. The same symbol in italics stands for the absolute value of the vector.

Note that the vectors \mathbf{a} , \mathbf{b} , \mathbf{c} define, not only the unit cell, but also the whole point lattice through the translations provided by these vectors. In other words, the whole set of points in the lattice can be produced by repeated action of the vectors \mathbf{a} , \mathbf{b} , \mathbf{c} on one lattice point located at the origin, or, stated alternatively, the vector coordinates of any point in the lattice are $P\mathbf{a}$, $Q\mathbf{b}$, and $R\mathbf{c}$, where P , Q , and R are whole numbers. It follows that the arrangement of points in a point lattice is absolutely periodic in three dimensions, points being repeated at regular intervals along any line one chooses to draw through the lattice.

2-3 CRYSTAL SYSTEMS

In dividing space by three sets of planes, we can of course produce unit cells of various shapes, depending on how we arrange the planes. For example, if the planes in the three sets are all equally spaced and mutually perpendicular, the unit cell is cubic. In this case the vectors \mathbf{a} , \mathbf{b} , \mathbf{c} are all equal and at right angles to one another, or $a = b = c$ and $\alpha = \beta = \gamma = 90^\circ$. By thus giving special values to the axial lengths and angles, we can produce unit cells of various shapes and therefore various kinds of point lattices, since the points of the lattice are located at the cell corners. It turns out that only seven different kinds of cells are necessary to include all the possible point lattices. These correspond to the seven *crystal systems* into which all crystals can be classified. These systems are listed in Table 2-1. (Some writers consider the rhombohedral system as a subdivision of the hexagonal, thus reducing the number of crystal systems to six.)

Seven different point lattices can be obtained simply by putting points at the corners of the unit cells of the seven crystal systems. However, there are other arrangements of points which fulfill the requirements of a point lattice, namely, that each point have identical surroundings. The French crystallographer Bravais worked on this problem and in 1848 demonstrated that there are fourteen possible point lattices and no more; this important result is commemorated by our use of the terms *Bravais lattice* and *point lattice* as synonymous. For example, if a point is placed at the center of each cell of a cubic point lattice, the new array of points also forms a point lattice. Similarly, another point lattice can be based on a cubic unit cell having lattice points at each corner and in the center of each face.

The fourteen Bravais lattices are described in Table 2-1 and illustrated in Fig. 2-3, where the symbols P , F , I , etc., have the following meanings. We must first distinguish between *simple*, or *primitive*, cells (symbol P or R) and *non-primitive* cells (any other symbol): primitive cells have only one lattice point per cell while nonprimitive have more than one. A lattice point in the interior of a cell "belongs" to that cell, while one in a cell face is shared by two cells and one at a corner is shared by eight. The number of lattice points per cell is therefore given by

$$N = N_i + \frac{N_f}{2} + \frac{N_c}{8}, \quad (2-1)$$

where N_i = number of interior points, N_f = number of points on faces, and N_c = number of points on corners. Any cell containing lattice points on the

Table 2-1
Crystal Systems and Bravais Lattices

(The symbol \neq means that equality is not required by symmetry. Accidental equality may occur, as shown by an example in Sec. 2-4.)

System	Axial lengths and angles	Bravais lattice	Lattice symbol
Cubic	Three equal axes at right angles $a = b = c, \alpha = \beta = \gamma = 90^\circ$	Simple Body-centered Face-centered	P I F
Tetragonal	Three axes at right angles, two equal $a = b \neq c, \alpha = \beta = \gamma = 90^\circ$	Simple Body-centered	P I
Orthorhombic	Three unequal axes at right angles $a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$	Simple Body-centered Base-centered Face-centered	P I C F
Rhombohedral*	Three equal axes, equally inclined $a = b = c, \alpha = \beta = \gamma \neq 90^\circ$	Simple	R
Hexagonal	Two equal coplanar axes at 120° , third axis at right angles $a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$	Simple	P
Monoclinic	Three unequal axes, one pair not at right angles $a \neq b \neq c, \alpha = \gamma = 90^\circ \neq \beta$	Simple Base-centered	P C
Triclinic	Three unequal axes, unequally inclined and none at right angles $a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$	Simple	P

* Also called trigonal.

corners only is therefore primitive, while one containing additional points in the interior or on faces is nonprimitive. The symbols *F* and *I* refer to face-centered and body-centered cells, respectively, while *A*, *B*, and *C* refer to base-centered cells, centered on one pair of opposite faces *A*, *B*, or *C*. (The *A* face is the face defined by the *b* and *c* axes, etc.) The symbol *R* is used especially for the rhombohedral system. In Fig. 2-3, axes of equal length in a particular system are given the same symbol to indicate their equality, e.g., the cubic axes are all marked *a*, the two equal tetragonal axes are marked *a* and the third one *c*, etc.

At first glance, the list of Bravais lattices in Table 2-1 appears incomplete. Why not, for example, a base-centered tetragonal lattice? The full lines in Fig. 2-4 delineate such a cell, centered on the *C* face, but we see that the same array of lattice points can be referred to the simple tetragonal cell shown by dashed lines, so that the base-centered arrangement of points is not a new lattice. However, the base-centered cell is a perfectly good unit cell and, if we wish, we may choose to use it rather than the simple cell. Choice of one or the other has certain consequences, which are described later (Problem 4-3).

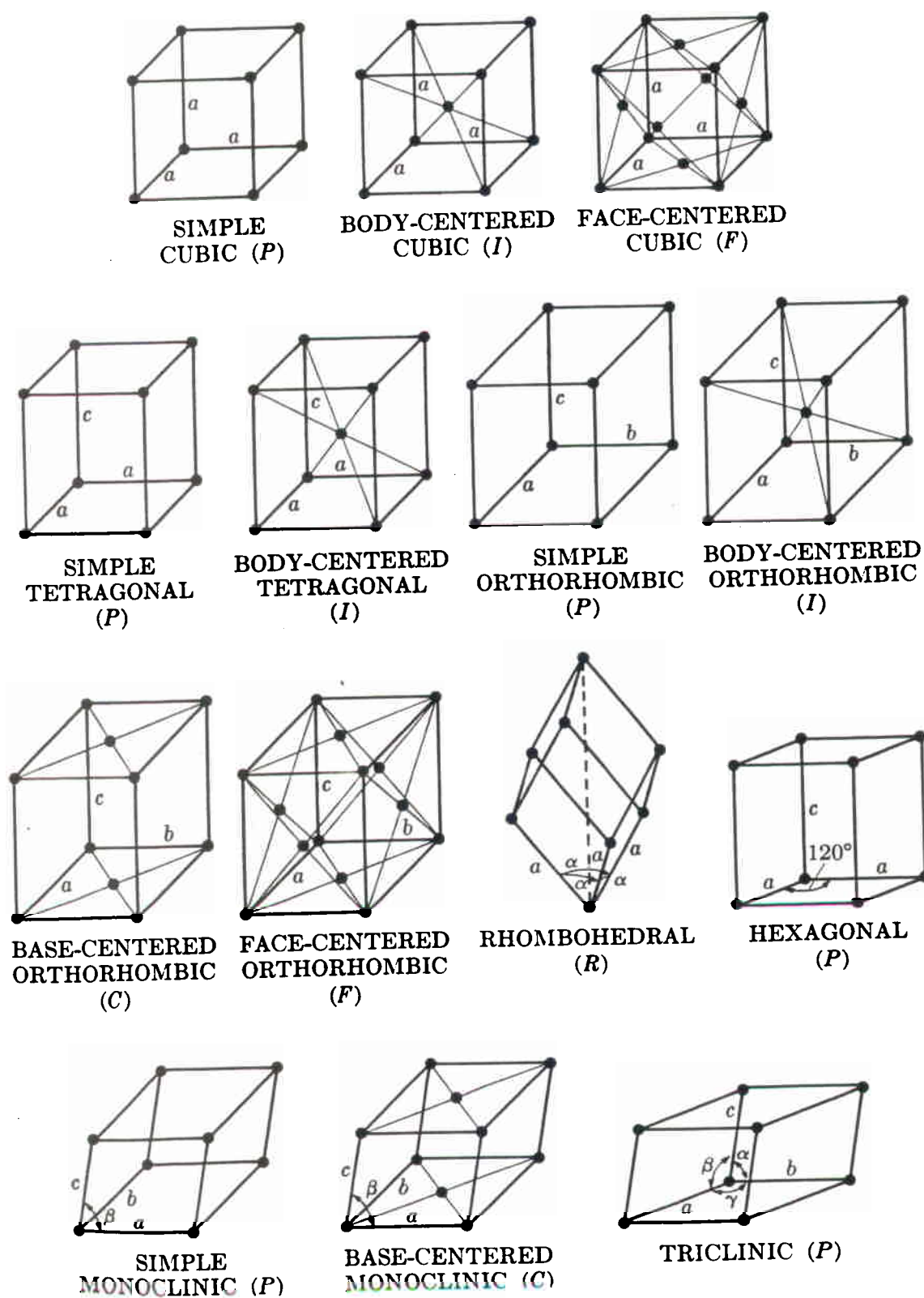


Fig. 2-3 The fourteen Bravais lattices.

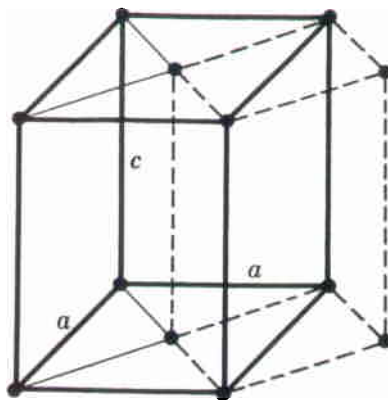


Fig. 2-4 Relation of tetragonal *C* lattice (full lines) to tetragonal *P* lattice (dashed lines).

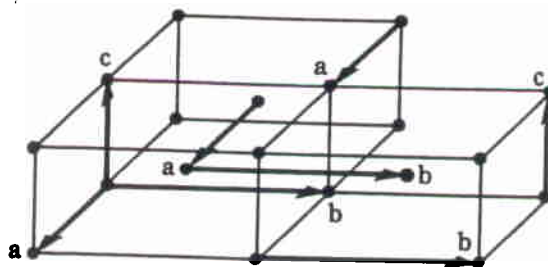


Fig. 2-5 Extension of lattice points through space by the unit cell vectors *a*, *b*, *c*.

The lattice points in a nonprimitive unit cell can be extended through space by repeated applications of the unit-cell vectors *a*, *b*, *c* just like those of a primitive cell. We may regard the lattice points associated with a unit cell as being translated one by one or as a group. In either case, equivalent lattice points in adjacent unit cells are separated by one of the vectors *a*, *b*, *c*, wherever these points happen to be located in the cell (Fig. 2-5).

2-4 SYMMETRY

Both Bravais lattices and the real crystals which are built up on them exhibit various kinds of symmetry. A body or structure is said to be symmetrical when its component parts are arranged in such balance, so to speak, that certain operations can be performed on the body which will bring it into coincidence with itself. These are termed *symmetry operations*. For example, if a body is symmetrical with respect to a plane passing through it, then reflection of either half of the body in the plane as in a mirror will produce a body coinciding with the other half. Thus a cube has several planes of symmetry, one of which is shown in Fig. 2-6(a).

There are in all four macroscopic* symmetry operations or elements: *reflection*,

* So called to distinguish them from certain microscopic symmetry operations with which we are not concerned here. The macroscopic elements can be deduced from the angles between the faces of a well-developed crystal, without any knowledge of the atom arrangement inside the crystal. The microscopic symmetry elements, on the other hand, depend entirely on atom arrangement, and their presence cannot be inferred from the external development of the crystal.

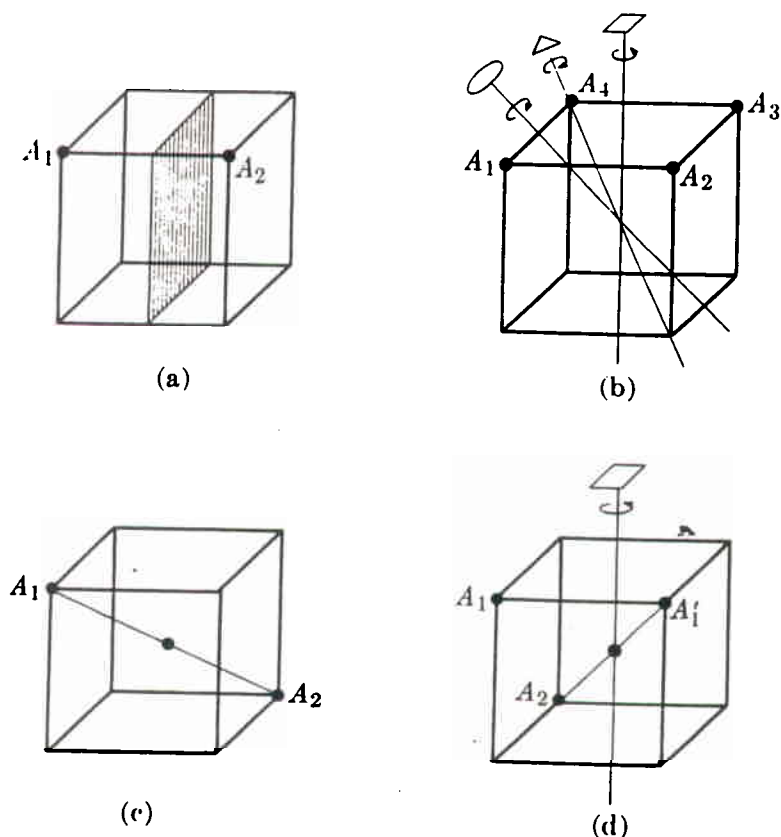


Fig. 2-6 Some symmetry elements of a cube. (a) Reflection plane. A_1 becomes A_2 . (b) Rotation axes. 4-fold axis: A_1 becomes A_2 ; 3-fold axis: A_1 becomes A_3 ; 2-fold axis: A_1 becomes A_4 . (c) Inversion center. A_1 becomes A_2 . (d) Rotation-inversion axis. 4-fold axis: A_1 becomes A_1' ; inversion center: A_1' becomes A_2 .

rotation, inversion, and rotation-inversion. A body has n -fold rotational symmetry about an axis if a rotation of $360^\circ/n$ brings it into self-coincidence. Thus a cube has a 4-fold rotation axis normal to each face, a 3-fold axis along each body diagonal, and 2-fold axes joining the centers of opposite edges. Some of these are shown in Fig. 2-6(b) where the small plane figures (square, triangle, and ellipse) designate the various kinds of axes. In general, rotation axes may be 1-, 2-, 3-, 4-, or 6-fold. A 1-fold axis indicates no symmetry at all, while a 5-fold axis or one of higher degree than 6 is impossible, in the sense that unit cells having such symmetry cannot be made to fill up space without leaving gaps.

A body has an inversion center if corresponding points of the body are located at equal distances from the center on a line drawn through the center. A body having an inversion center will come into coincidence with itself if every point in the body is inverted, or "reflected," in the inversion center. A cube has such a center at the intersection of its body diagonals [Fig. 2-6(c)]. Finally, a body may have a rotation-inversion axis, either 1-, 2-, 3-, 4-, or 6-fold. If it has an n -fold rotation-inversion axis, it can be brought into coincidence with itself by a rotation of $360^\circ/n$ about the axis followed by inversion in a center lying on the axis. Figure 2-6(d) illustrates the operation of a 4-fold rotation-inversion axis on a cube.

Now, the possession of a certain minimum set of symmetry elements is a

Table 2-2
Symmetry Elements

System	Minimum symmetry elements
Cubic	Four 3-fold rotation axes
Tetragonal	One 4-fold rotation (or rotation - inversion) axis
Orthorhombic	Three perpendicular 2-fold rotation (or rotation - inversion) axes
Rhombohedral	One 3-fold rotation (or rotation - inversion) axis
Hexagonal	One 6-fold rotation (or rotation - inversion) axis
Monoclinic	One 2-fold rotation (or rotation - inversion) axis
Triclinic	None

fundamental property of each crystal system, and one system is distinguished from another just as much by its symmetry elements as by the values of its axial lengths and angles. In fact, *these are interdependent*. For example, the existence of 4-fold rotation axes normal to the faces of a cubic cell *requires* that the cell edges be equal in length and at 90° to one another. On the other hand, a tetragonal cell has only one 4-fold axis, and this symmetry requires that only two cell edges be equal, namely, the two that are at right angles to the rotation axis.

The minimum number of symmetry elements possessed by each crystal system is listed in Table 2-2. Some crystals may possess more than the minimum symmetry elements required by the system to which they belong, but none may have less. The existence of certain symmetry elements often implies the existence of others. For example, a crystal with three 4-fold rotation axes necessarily has, in addition, four 3-fold axes and falls in the cubic system.

Symmetry operations apply not only to the unit cells shown in Fig. 2-3, considered merely as geometric shapes, but also to the point lattices associated with them. The latter condition rules out the possibility that the cubic system, for example, could include a base-centered point lattice, since such an array of points would not have the minimum set of symmetry elements required by the cubic system, namely four 3-fold rotation axes. Such a lattice would be classified in the tetragonal system, which has no 3-fold axes and in which accidental equality of the a and c axes is allowed.

Crystals in the rhombohedral (trigonal) system can be referred to either a rhombohedral or a hexagonal lattice. Appendix 4 gives the relation between these two lattices and the transformation equations which allow the Miller indices of a plane (see Sec. 2-6) to be expressed in terms of either set of axes.

2-5 PRIMITIVE AND NONPRIMITIVE CELLS

In any point lattice a unit cell may be chosen in an infinite number of ways and may contain one or more lattice points per cell. It is important to note that unit cells do not "exist" as such in a lattice: they are a mental construct and can

accordingly be chosen at our convenience. The conventional cells shown in Fig. 2-3 are chosen simply for convenience and to conform to the symmetry elements of the lattice.

Any of the fourteen Bravais lattices may be referred to a primitive unit cell. For example, the face-centered cubic lattice shown in Fig. 2-7 may be referred to the primitive cell indicated by dashed lines. The latter cell is rhombohedral, its axial angle α is 60° , and each of its axes is $1/\sqrt{2}$ times the length of the axes of the cubic cell. Each cubic cell has four lattice points associated with it, each rhombohedral cell has one, and the former has, correspondingly, four times the volume of the latter. Nevertheless, it is usually more convenient to use the cubic cell rather than the rhombohedral one because the former immediately suggests the cubic symmetry which the lattice actually possesses. Similarly, the other centered nonprimitive cells listed in Table 2-1 are preferred to the primitive cells possible in their respective lattices.

Why then do the centered lattices appear in the list of the fourteen Bravais lattices? If the two cells in Fig. 2-7 describe the same set of lattice points, as they do, why not eliminate the cubic cell and let the rhombohedral cell serve instead? The answer is that this cell is a *particular* rhombohedral cell with an axial angle α of 60° . In the general rhombohedral lattice no restriction is placed on the angle α ; the result is a lattice of points with a single 3-fold symmetry axis. When α becomes equal to 60° , the lattice has four 3-fold axes, and this symmetry places it in the cubic system. The general rhombohedral cell is still needed.

If nonprimitive lattice cells are used, the vector from the origin to any point in the lattice will now have components which are nonintegral multiples of the unit-cell vectors \mathbf{a} , \mathbf{b} , \mathbf{c} . The position of any lattice point in a cell may be given in terms of its *coordinates*; if the vector from the origin of the unit cell to the given point has components $x\mathbf{a}$, $y\mathbf{b}$, $z\mathbf{c}$, where x , y , and z are fractions, then the coordinates of the point are $x\ y\ z$. Thus, point A in Fig. 2-7, taken as the origin, has coordinates $0\ 0\ 0$ while points B , C , and D , when referred to cubic axes, have coordinates $0\ \frac{1}{2}\ \frac{1}{2}$, $\frac{1}{2}\ 0\ \frac{1}{2}$, and $\frac{1}{2}\ \frac{1}{2}\ 0$, respectively. Point E has coordinates $\frac{1}{2}\ \frac{1}{2}\ 1$ and is equivalent to point D , being separated from it by the vector \mathbf{c} . The coordinates

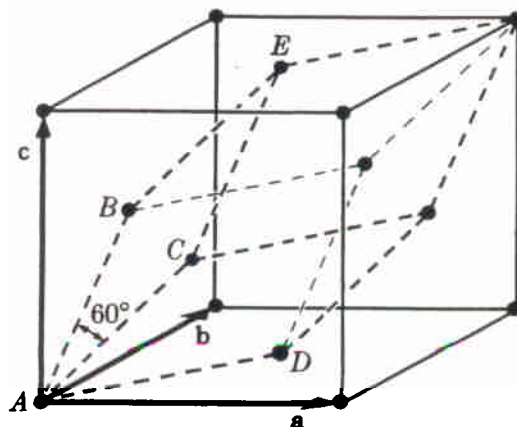


Fig. 2-7 Face-centered cubic point lattice referred to cubic and rhombohedral cells.

of equivalent points in different unit cells can always be made identical by the addition or subtraction of a set of integral coordinates; in this case, subtraction of 0 0 1 from $\frac{1}{2} \frac{1}{2} 1$ (the coordinates of *E*) gives $\frac{1}{2} \frac{1}{2} 0$ (the coordinates of *D*).

Note that the coordinates of a body-centered point, for example, are always $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ no matter whether the unit cell is cubic, tetragonal, or orthorhombic, and whatever its size. The coordinates of a point position, such as $\frac{1}{2} \frac{1}{2} \frac{1}{2}$, may also be regarded as an operator which, when "applied" to a point at the origin, will move or translate it to the position $\frac{1}{2} \frac{1}{2} \frac{1}{2}$, the final position being obtained by simple addition of the operator $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ and the original position 0 0 0. In this sense, the positions 0 0 0, $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ are called the "body-centering translations," since they will produce the two point positions characteristic of a body-centered cell when applied to a point at the origin. Similarly, the four point positions characteristic of a face-centered cell, namely, 0 0 0, $0 \frac{1}{2} \frac{1}{2}$, $\frac{1}{2} 0 \frac{1}{2}$, and $\frac{1}{2} \frac{1}{2} 0$, are called the face-centering translations. The base-centering translations depend on which pair of opposite faces are centered; if centered on the *C* face, for example, they are 0 0 0, $\frac{1}{2} \frac{1}{2} 0$. These centering translations, summarized below, should be memorized:

$$\begin{aligned}\text{body-centering} &= 0\ 0\ 0, \frac{1}{2}\ \frac{1}{2}\ \frac{1}{2} \\ \text{face-centering} &= 0\ 0\ 0, 0\ \frac{1}{2}\ \frac{1}{2}, \frac{1}{2}\ 0\ \frac{1}{2}, \frac{1}{2}\ \frac{1}{2}\ 0 \\ \text{base-centering} &= 0\ 0\ 0, \frac{1}{2}\ \frac{1}{2}\ 0.\end{aligned}$$

The inclusion of 0 0 0 may appear trivial, in that it does not move the point at the origin on which it acts, but its inclusion does remind us that cells so centered contain 2, 4, and 2 lattice points, respectively.

2-6 LATTICE DIRECTIONS AND PLANES

The direction of any line in a lattice may be described by first drawing a line through the origin parallel to the given line and then giving the coordinates of any point on the line through the origin. Let the line pass through the origin of the unit cell and any point having coordinates *u v w*, where these numbers are not necessarily integral. (This line will also pass through the points *2u 2v 2w*, *3u 3v 3w*, etc.) Then [*uvw*], written in square brackets, are the *indices* of the direction of the line. They are also the indices of any line parallel to the given line, since the lattice is infinite and the origin may be taken at any point. Whatever the values of *u*, *v*, *w*, they are always converted to a set of smallest integers by multiplication or division throughout: thus, [$\frac{1}{2} \frac{1}{2} 1$], [112], and [224] all represent the same direction, but [112] is the preferred form. Negative indices are written with a bar over the number, e.g., [$\bar{u}vw$]. Direction indices are illustrated in Fig. 2-8. Note how one can mentally shift the origin, to avoid using the adjacent unit cell, in finding a direction like [$\bar{1}20$].

Directions related by symmetry are called *directions of a form*, and a set of these are represented by the indices of one of them enclosed in angular brackets; for example, the four body diagonals of a cube, [111], [$\bar{1}\bar{1}1$], [$\bar{1}1\bar{1}$], and [$1\bar{1}\bar{1}$], may all be represented by the symbol $\langle 111 \rangle$.

The orientation of planes in a lattice may also be represented symbolically, according to a system popularized by the English crystallographer Miller. In the

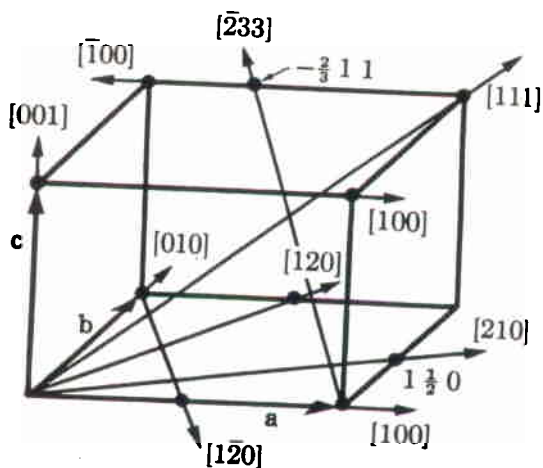


Fig. 2-8 Indices of directions.

general case, the given plane will be tilted with respect to the crystallographic axes, and, since these axes form a convenient frame of reference, we might describe the orientation of the plane by giving the actual distances, measured from the origin, at which it intercepts the three axes. Better still, by expressing these distances as fractions of the axial lengths, we can obtain numbers which are independent of the particular axial lengths involved in the given lattice. But a difficulty then arises when the given plane is parallel to a certain crystallographic axis, because such a plane does not intercept that axis, i.e., its "intercept" can only be described as "infinity." To avoid the introduction of infinity into the description of plane orientation, we can use the reciprocal of the fractional intercept, this reciprocal being zero when the plane and axis are parallel. We thus arrive at a workable symbolism for the orientation of a plane in a lattice, the *Miller indices*, which are defined as *the reciprocals of the fractional intercepts which the plane makes with the crystallographic axes*. For example, if the Miller indices of a plane are (hkl) , written in parentheses, then the plane makes fractional intercepts of $1/h$, $1/k$, $1/l$ with the axes, and, if the axial lengths are a , b , c , the plane makes actual intercepts of a/h , b/k , c/l , as shown in Fig. 2-9(a). Parallel to any plane in any lattice, there is a whole set of parallel equidistant planes, one of which passes through the origin; the Miller indices (hkl) usually refer to that plane in the set which is nearest the origin, although they may be taken as referring to any other plane in the set or to the whole set taken together.

We may determine the Miller indices of the plane shown in Fig. 2-9(b) as follows:

Axial lengths	4 Å	8 Å	3 Å
Intercept lengths	1 Å	4 Å	3 Å
Fractional intercepts	$\frac{1}{4}$	$\frac{1}{2}$	1
Miller indices	4	2	1

As stated earlier, if a plane is parallel to a given axis, its fractional intercept on that axis is taken as infinity and the corresponding Miller index is zero. If a plane cuts

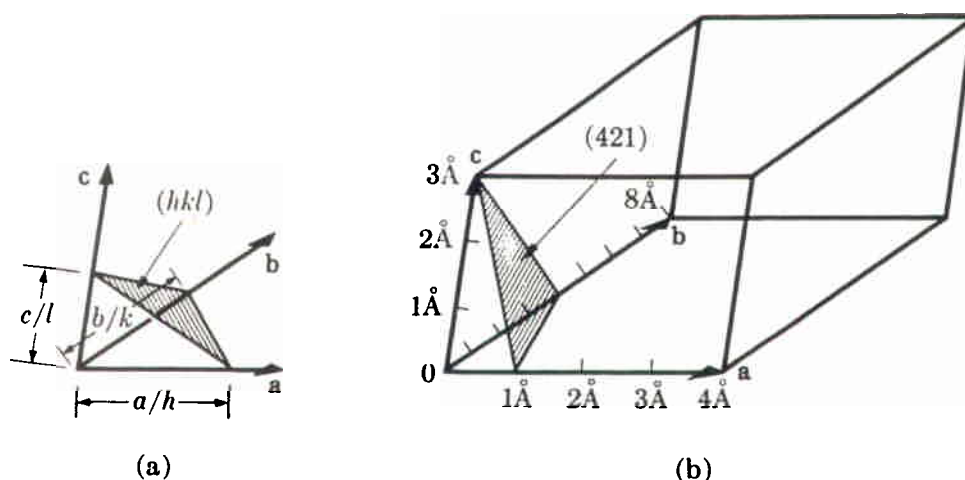


Fig. 2-9 Plane designation by Miller indices.

a negative axis, the corresponding index is negative and is written with a bar over it. Planes whose indices are the negatives of one another are parallel and lie on opposite sides of the origin, e.g., $(\bar{2}10)$ and $(2\bar{1}0)$. The planes $(nh\ nk\ nl)$ are parallel to the planes (hkl) and have $1/n$ th the spacing. The same plane may belong to two different sets, the Miller indices of one set being multiples of those of the other; thus the same plane belongs to the (210) set and the (420) set, and, in fact, the planes of the (210) set form every second plane in the (420) set. In the cubic system, it is convenient to remember that a direction $[hkl]$ is always perpendicular to a plane (hkl) of the same indices, but this is not generally true in other systems. Further familiarity with Miller indices can be gained from a study of Fig. 2-10.

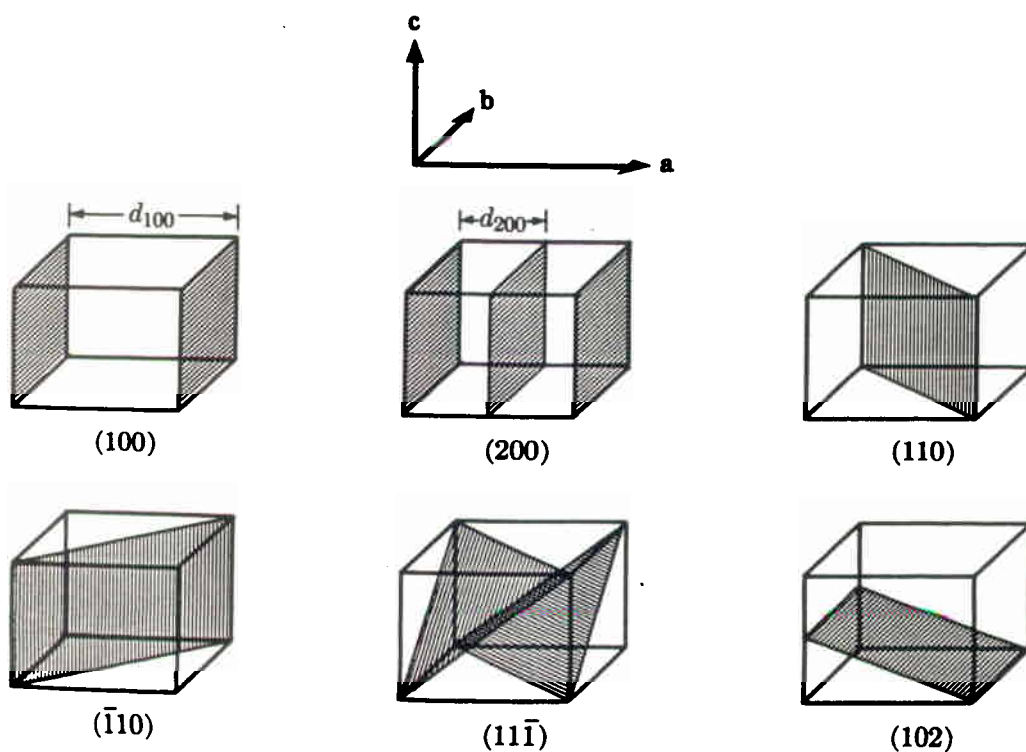


Fig. 2-10 Miller indices of lattice planes. The distance d is the plane spacing.

A slightly different system of plane indexing is used in the hexagonal system. The unit cell of a hexagonal lattice is defined by two equal and coplanar vectors \mathbf{a}_1 and \mathbf{a}_2 , at 120° to one another, and a third axis \mathbf{c} at right angles [Fig. 2-11(a)]. The complete lattice is built up, as usual, by repeated translations of the points at the unit cell corners by the vectors \mathbf{a}_1 , \mathbf{a}_2 , \mathbf{c} . Some of the points so generated are shown in the figure, at the ends of dashed lines, in order to exhibit the hexagonal symmetry of the lattice, which has a 6-fold rotation axis parallel to \mathbf{c} . The third axis \mathbf{a}_3 , lying in the basal plane of the hexagonal prism, is so symmetrically related to \mathbf{a}_1 and \mathbf{a}_2 that it is often used in conjunction with the other two. Thus the indices of a plane in the hexagonal system, called Miller-Bravais indices, refer to *four* axes and are written $(hkil)$. The index i is the reciprocal of the fractional intercept on the \mathbf{a}_3 axis. Since the intercepts of a plane on \mathbf{a}_1 and \mathbf{a}_2 determine its intercept on \mathbf{a}_3 , the value of i depends on the values of h and k . The relation is

$$h + k = -i. \quad (2-2)$$

Since i is determined by h and k , it is sometimes replaced by a dot and the plane symbol written $(hk \cdot l)$. Sometimes even the dot is omitted. However, this usage defeats the purpose for which Miller-Bravais indices were devised, namely, to give similar indices to similar planes. For example, the side planes of the hexagonal prism in Fig. 2-11(b) are all similar and symmetrically located, and their relationship is clearly shown in their full Miller-Bravais symbols: $(10\bar{1}0)$, $(01\bar{1}0)$, $(\bar{1}100)$, $(\bar{1}010)$, $(0\bar{1}10)$, $(1\bar{1}00)$. On the other hand, the abbreviated symbols of these planes, $(10 \cdot 0)$, $(01 \cdot 0)$, $(\bar{1}1 \cdot 0)$, $(\bar{1}0 \cdot 0)$, $(0\bar{1} \cdot 0)$, $(1\bar{1} \cdot 0)$ do not immediately suggest this relationship.

Directions in a hexagonal lattice are best expressed in terms of the *three* basic vectors \mathbf{a}_1 , \mathbf{a}_2 , and \mathbf{c} . Figure 2-11(b) shows several examples of both plane and direction indices. Another system, involving four indices, is sometimes used to designate directions. The required direction is broken up into four component vectors, parallel to \mathbf{a}_1 , \mathbf{a}_2 , \mathbf{a}_3 , and \mathbf{c} and so chosen that the third index is the

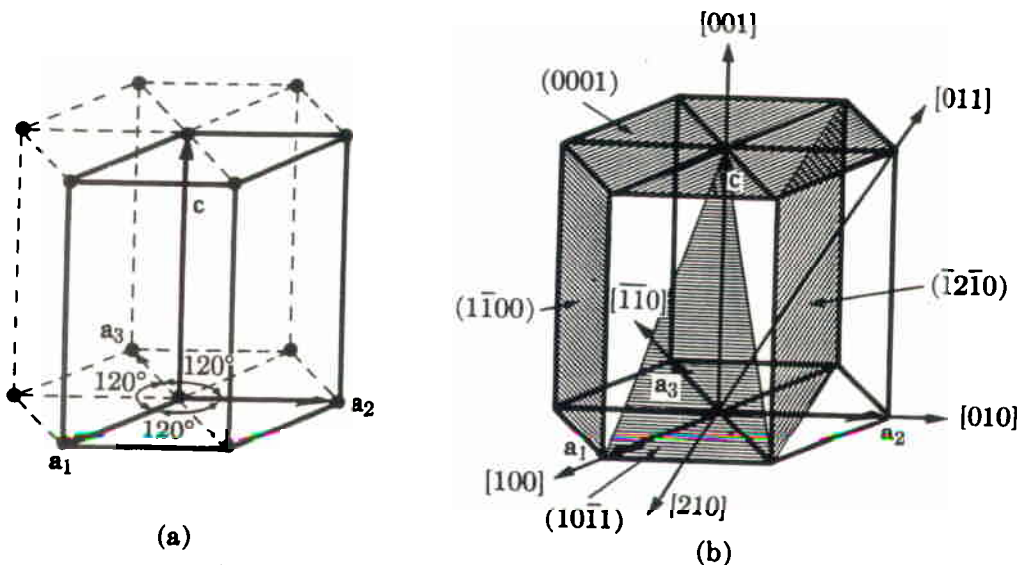


Fig. 2-11 (a) The hexagonal unit cell (heavy lines) and (b) indices of planes and directions.

negative of the sum of the first two. Then, if $[UVW]$ are the indices of a direction referred to three axes and $[uvw]$ the four-axis indices, the two are related as follows:

$$\begin{aligned} U &= u - t & u &= (2U - V)/3 \\ V &= v - t & v &= (2V - U)/3 \\ W &= w & t &= -(u + v) = -(U + V)/3 \\ & & w &= W. \end{aligned}$$

Thus, $[100]$ becomes $[2\bar{1}0]$, $[210]$ becomes $[10\bar{1}0]$, etc.

Note that the indices of a plane or direction are meaningless unless the orientation of the unit-cell axes is given. This means that the indices of a particular lattice plane depend on the unit cell chosen. For example, consider the right-hand vertical plane of the cell shown by full lines in Fig. 2-4; the indices of this plane are of the form $\{100\}$ for the base-centered cell and $\{110\}$ for the simple cell.

In any crystal system there are sets of equivalent lattice planes related by symmetry. These are called *planes of a form*, and the indices of any one plane, enclosed in braces $\{hkl\}$, stand for the whole set. In general, planes of a form have the same spacing but different Miller indices. For example, the faces of a cube, (100) , (010) , $(\bar{1}00)$, $(0\bar{1}0)$, (001) , and $(00\bar{1})$, are planes of the form $\{100\}$, since all of them may be generated from any one by operation of the 4-fold rotation axes perpendicular to the cube faces. In the tetragonal system, however, only the planes (100) , (010) , $(\bar{1}00)$, and $(0\bar{1}0)$ belong to the form $\{100\}$; the other two planes, (001) and $(00\bar{1})$, belong to the different form $\{001\}$; the first four planes mentioned are related by a 4-fold axis and the last two by a 2-fold axis.*

Planes of a zone are planes which are all parallel to one line, called the *zone axis*, and the zone, i.e., the set of planes, is specified by giving the indices of the zone axis. Such planes may have quite different indices and spacings, the only requirement being their parallelism to a line. Figure 2-12 shows some examples. If the axis of a zone has indices $[uvw]$, then any plane belongs to that zone whose indices (hkl) satisfy the relation

$$hu + kv + lw = 0. \quad (2-3)$$

(A proof of this relation is given in Sec. 3 of Appendix 1.) Any two nonparallel planes are planes of a zone since they are both parallel to their line of intersection. If their indices are $(h_1k_1l_1)$ and $(h_2k_2l_2)$, then the indices of their zone axis $[uvw]$ are given by the relations

$$\begin{aligned} u &= k_1l_2 - k_2l_1, \\ v &= l_1h_2 - l_2h_1, \\ w &= h_1k_2 - h_2k_1. \end{aligned} \quad (2-4)$$

* Certain important crystal planes are often referred to by name without any mention of their Miller indices. Thus, planes of the form $\{111\}$ in the cubic system are often called octahedral planes, since these are the bounding planes of an octahedron. In the hexagonal system, the (0001) plane is called the basal plane, planes of the form $\{10\bar{1}0\}$ are called prismatic planes, and planes of the form $\{10\bar{1}1\}$ are called pyramidal planes.

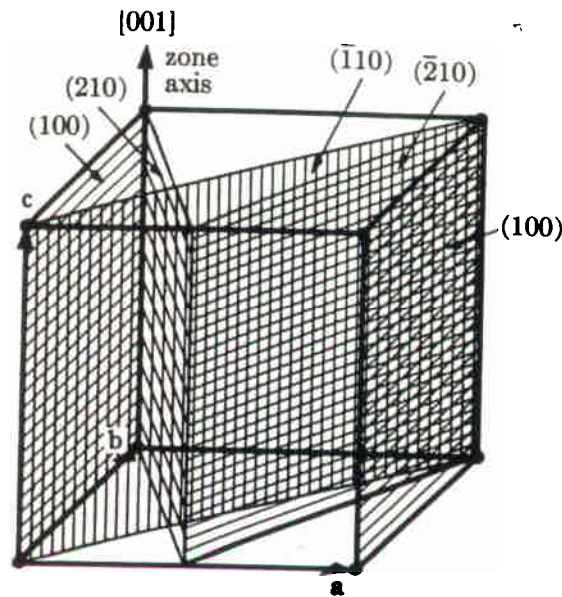


Fig. 2-12 All shaded planes in the cubic lattice shown are planes of the zone $[001]$.

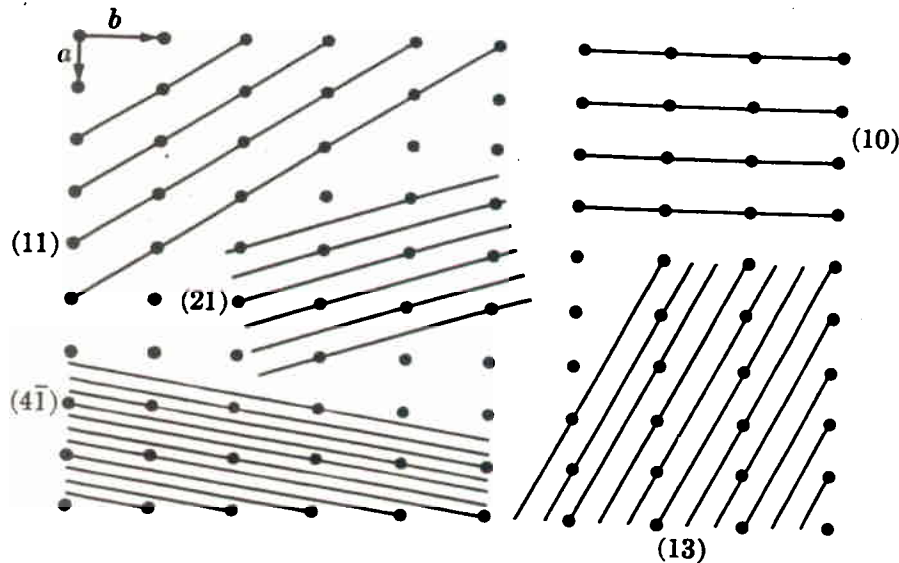


Fig. 2-13 Two-dimensional lattice, showing that lines of lowest indices have the greatest spacing and the greatest density of lattice points.

The various sets of planes in a lattice have various values of interplanar spacing. The planes of large spacing have low indices and pass through a high density of lattice points, whereas the reverse is true of planes of small spacing. Figure 2-13 illustrates this for a two-dimensional lattice, and it is equally true in three dimensions. The interplanar spacing d_{hkl} , measured at right angles to the planes, is a function both of the plane indices (hkl) and the lattice constants ($a, b, c, \alpha, \beta, \gamma$). The exact relation depends on the crystal system involved and for the cubic system takes on the relatively simple form

$$\text{(Cubic)} \quad d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}. \quad (2-5)$$

In the tetragonal system the spacing equation naturally involves both a and c since these are not generally equal:

$$\text{(Tetragonal)} \quad d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2 (a^2/c^2)}}. \quad (2-6)$$

Interplanar spacing equations for all systems are given in Appendix 3.

2-7 CRYSTAL STRUCTURE

So far we have discussed topics from the field of *mathematical (geometrical) crystallography* and have said practically nothing about actual crystals and the atoms of which they are composed. In fact, all of the above was well known long before the discovery of x-ray diffraction, i.e., long before there was any certain knowledge of the interior arrangements of atoms in crystals.

It is now time to describe the structure of some actual crystals and to relate this structure to the point lattices, crystal systems, and symmetry elements discussed above. The cardinal principle of crystal structure is that *the atoms of a crystal are set in space either on the points of a Bravais lattice or in some fixed relation to those points*. It follows from this that the atoms of a crystal will be arranged periodically in three dimensions and that this arrangement of atoms will exhibit many of the properties of a Bravais lattice, in particular many of its symmetry elements.

The simplest crystals one can imagine are those formed by placing atoms of the same kind *on* the points of a Bravais lattice. Not all such crystals exist but, fortunately for metallurgists, many metals crystallize in this simple fashion, and Fig. 2-14 shows two common structures based on the body-centered cubic (BCC) and face-centered cubic (FCC) lattices. The former has two atoms per unit cell and the latter four, as we can find by rewriting Eq. (2-1) in terms of the number of atoms, rather than lattice points, per cell and applying it to the unit cells shown.

The next degree of complexity is encountered when two or more atoms of the same kind are "associated with" each point of a Bravais lattice, as exemplified by the hexagonal close-packed (HCP) structure common to many metals. This structure is simple hexagonal and is illustrated in Fig. 2-15. There are two atoms per unit cell, as shown in (a), one at 0 0 0 and the other at $\frac{2}{3} \frac{1}{3} \frac{1}{2}$ (or at $\frac{1}{3} \frac{2}{3} \frac{1}{2}$, which is an equivalent position). Figure 2-15(b) shows the same structure with the origin of the unit cell shifted so that the point 1 0 0 in the new cell is midway between

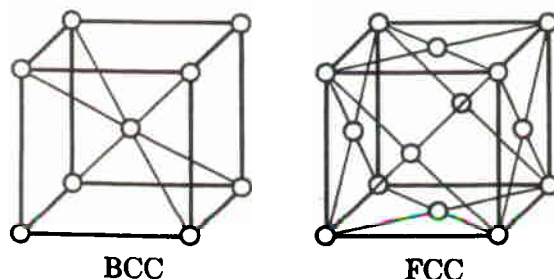


Fig. 2-14 Structures of some common metals. Body-centered cubic: α -Fe, Cr, Mo, V, etc.; face-centered cubic: γ -Fe, Cu, Pb, Ni, etc.

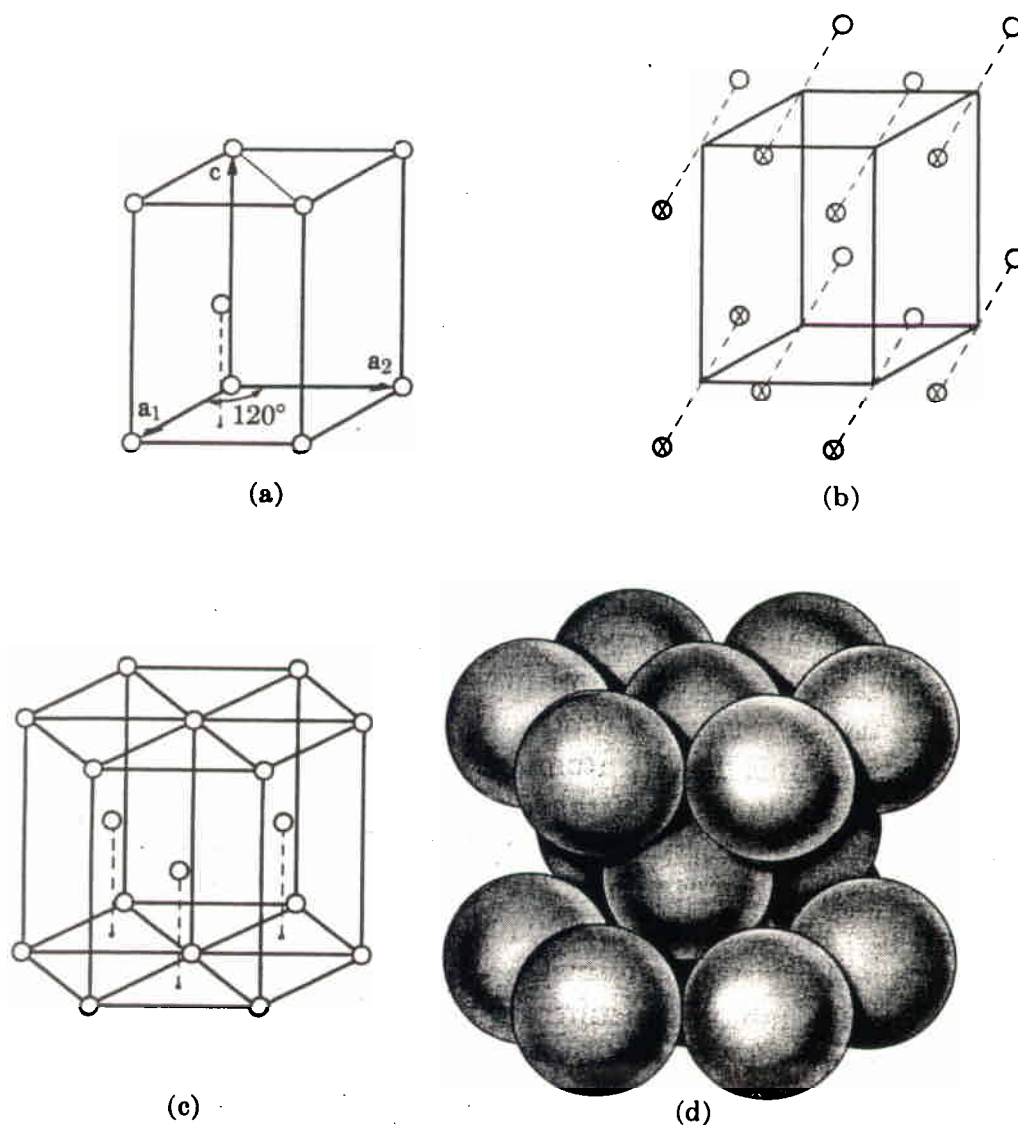


Fig. 2-15 The hexagonal close-packed structure, shared by Zn, Mg, Be, α -Ti, etc.

the atoms at $1\ 0\ 0$ and $\frac{2}{3}\ \frac{1}{3}\ \frac{1}{2}$ in (a), the nine atoms shown in (a) corresponding to the nine atoms marked with an X in (b). The “association” of pairs of atoms with the points of a simple hexagonal Bravais lattice is suggested by the dashed lines in (b). Note, however, that the atoms of a close-packed hexagonal structure do not themselves form a point lattice, the surroundings of an atom at $0\ 0\ 0$ being different from those of an atom at $\frac{2}{3}\ \frac{1}{3}\ \frac{1}{2}$. Figure 2-15(c) shows still another representation of the HCP structure: the three atoms in the interior of the hexagonal prism are directly above the centers of alternate triangles in the base and, if repeated through space by the vectors a_1 and a_2 , would also form a hexagonal array just like the atoms in the layers above and below.

The HCP structure is so called because it is one of the two ways in which spheres can be packed together in space with the greatest possible density and still have a periodic arrangement. Such an arrangement of spheres in contact is shown in Fig. 2-15(d). If these spheres are regarded as atoms, then the resulting picture of an HCP metal is much closer to physical reality than is the relatively open

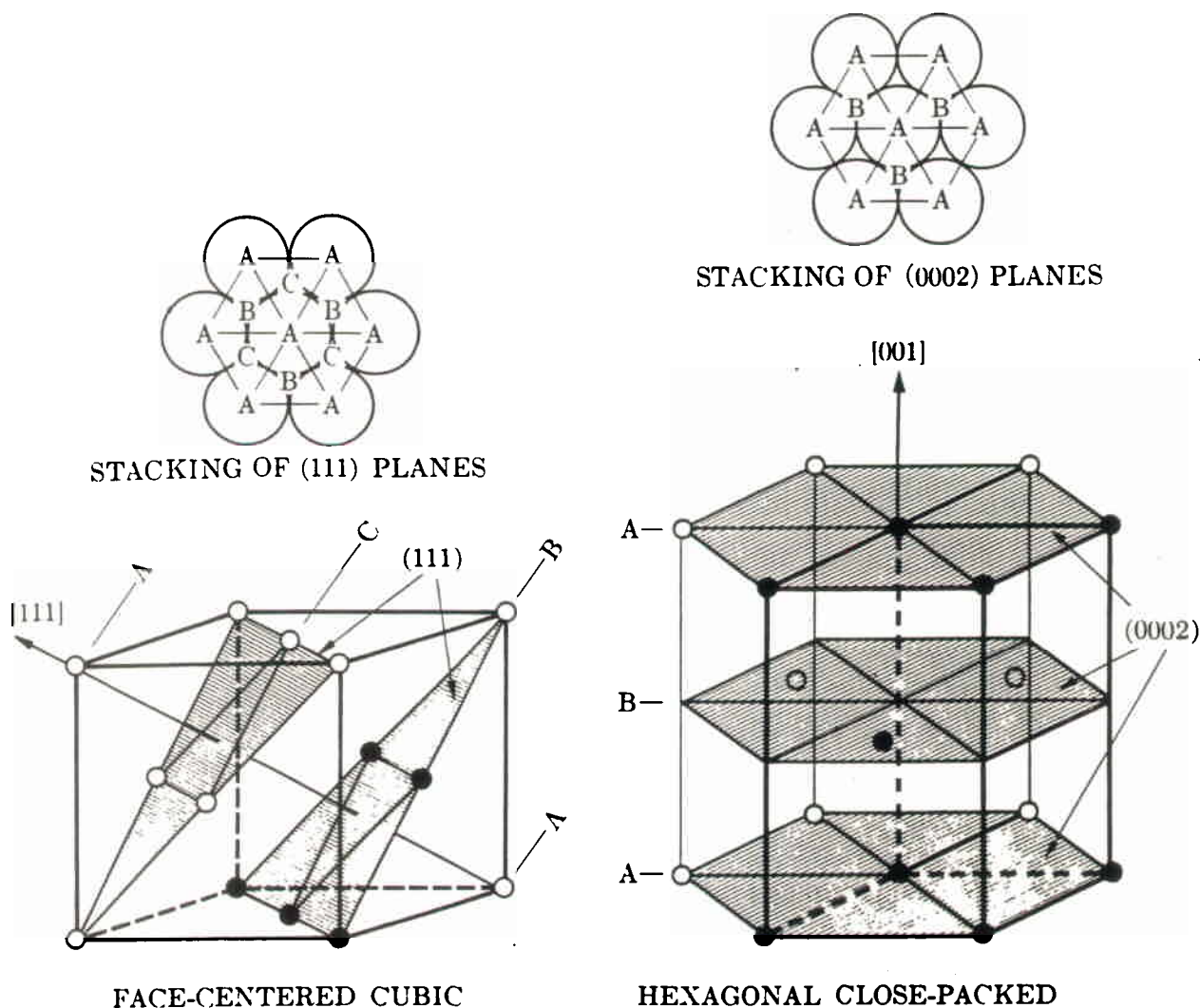


Fig. 2-16 Comparison of FCC and HCP structures. The black atoms in the FCC drawing delineate half a hexagon, which is completed on the same plane extended into the next unit cell below (not shown).

structure suggested by the drawing of Fig. 2-15(c), and this is true, generally, of all crystals. On the other hand, it may be shown that the ratio of c to a in an HCP structure formed of spheres in contact is 1.633 whereas the c/a ratio of metals having this structure varies from about 1.58 (Be) to 1.89 (Cd). As there is no reason to suppose that the atoms in these crystals are not in contact, it follows that they must be ellipsoidal in shape rather than spherical.

The FCC structure is an equally close-packed arrangement. Its relation to the HCP structure is not immediately obvious, but Fig. 2-16 shows that the atoms on the (111) planes of the FCC structure are arranged in a hexagonal pattern just like the atoms on the (0002) planes of the HCP structure. The only difference between the two structures is the way in which these hexagonal sheets of atoms are arranged above one another. In an HCP metal, the atoms in the second layer are above the hollows in the first layer and the atoms in the third layer are above the atoms in the first layer, so that the layer stacking sequence can be summarized as $ABABAB\dots$. The first two atom layers of an FCC metal are put down in the same way, but the atoms of the third layer are so placed in the hollows of the second

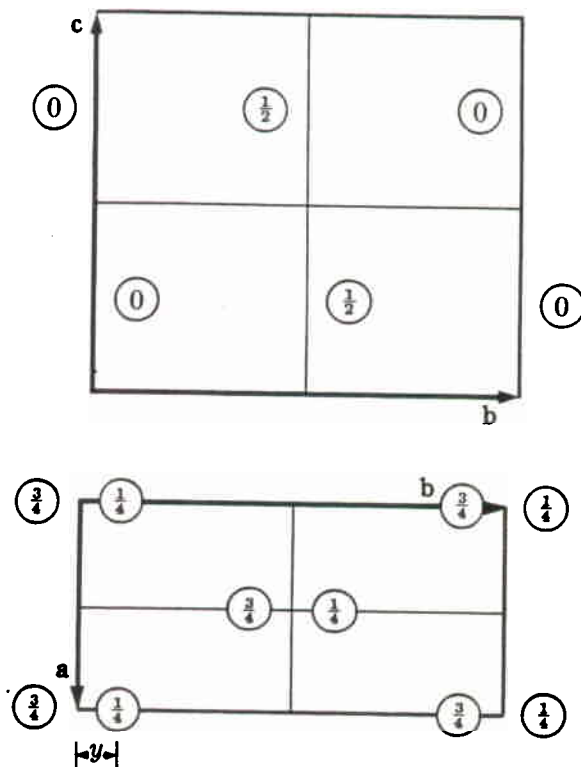


Fig. 2-17 The structure of α -uranium, after Jacob and Warren [2.1].

layer that not until the fourth layer does a position repeat. FCC stacking therefore has the sequence $A B C A B C \dots$. These stacking schemes are indicated in the plan views shown in Fig. 2-16.

Another example of the "association" of more than one atom with each point of a Bravais lattice is given by uranium. The structure of the form stable at room temperature, α -uranium, is illustrated in Fig. 2-17 by plan and elevation drawings. In such drawings, the height of an atom (expressed as a fraction of the axial length) above the plane of the drawing (which includes the origin of the unit cell and two of the cell axes) is given by the numbers marked on each atom. The Bravais lattice is base-centered orthorhombic, centered on the C face, and Fig. 2-17 shows how the atoms occur in pairs through the structure, each pair associated with a lattice point. There are four atoms per unit cell, located at $0 \ y \ \frac{1}{4}$, $0 \ \bar{y} \ \frac{3}{4}$, $\frac{1}{2} (\frac{1}{2} + y) \ \frac{1}{4}$, and $\frac{1}{2} (\frac{1}{2} - y) \ \frac{3}{4}$. Here we have an example of a variable parameter y in the atomic coordinates. Crystals often contain such variable parameters, which may have any fractional value without destroying any of the symmetry elements of the structure. A quite different substance might have exactly the same structure as uranium except for slightly different values of a , b , c , and y . For uranium y is 0.105 ± 0.005 .

Turning to the crystal structure of *compounds* of unlike atoms, we find that the structure is built up on the skeleton of a Bravais lattice but that certain other rules must be obeyed, precisely because there are unlike atoms present. Consider, for example, a crystal of A_xB_y , which might be an ordinary chemical compound, an intermediate phase of relatively fixed composition in some alloy system, or an ordered solid solution. Then the arrangement of atoms in A_xB_y must satisfy the

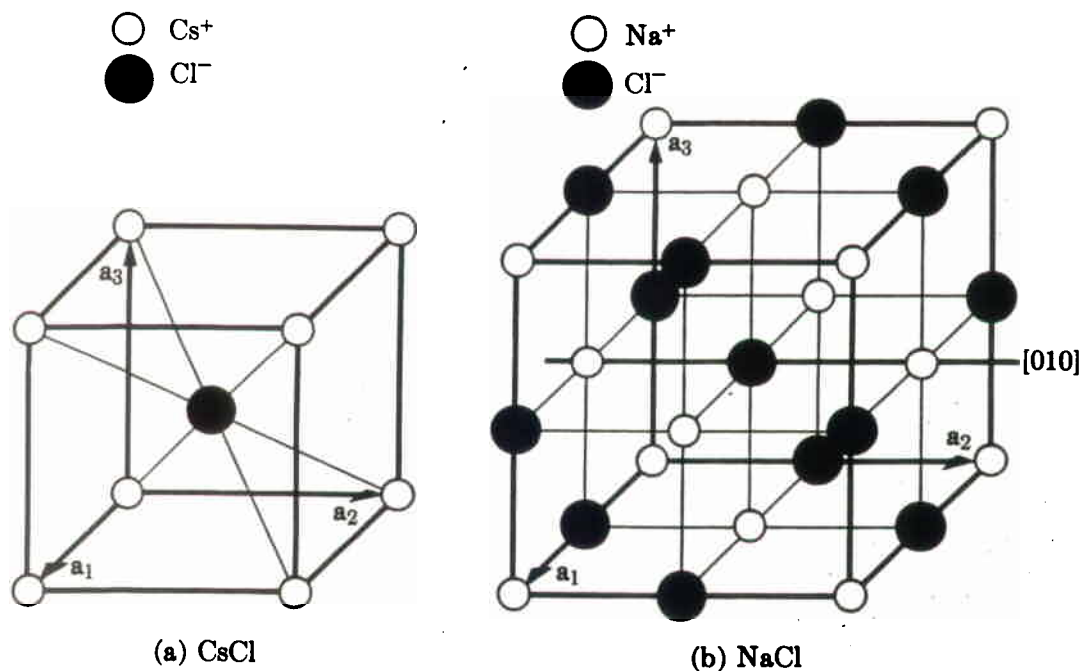


Fig. 2-18 The structures of (a) CsCl (common to CsBr, NiAl, ordered β -brass, ordered CuPd, etc.) and (b) NaCl (common to KCl, CaSe, PbTe, etc.).

following conditions:

1. Body-, face-, or base-centering translations, if present, must begin and end on atoms of the same kind. For example, if the structure is based on a body-centered Bravais lattice, then it must be possible to go from an A atom, say, to *another* A atom by the translation $\frac{1}{2} \frac{1}{2} \frac{1}{2}$.
2. The set of A atoms in the crystal and the set of B atoms must separately possess the same symmetry elements as the crystal as a whole, since in fact they make up the crystal. In particular, the operation of any symmetry element present must bring a given atom, A for example, into coincidence with another atom of the same kind, namely A.

Suppose we consider the structures of a few common crystals in light of the above requirements. Figure 2-18 illustrates the unit cells of two ionic compounds, CsCl and NaCl. These structures, both cubic, are common to many other crystals and, wherever they occur, are referred to as the "CsCl structure" and the "NaCl structure." In considering a crystal structure, one of the most important things to determine is its Bravais lattice, since that is the basic framework on which the crystal is built and because, as we shall see later, it has a profound effect on the way in which that crystal diffracts x-rays.

What is the Bravais lattice of CsCl? Figure 2-18(a) shows that the unit cell contains two atoms, ions really, since this compound is completely ionized even in the solid state: a caesium ion at 0 0 0 and a chlorine ion at $\frac{1}{2} \frac{1}{2} \frac{1}{2}$. The Bravais lattice is obviously not face-centered, but we note that the body-centering translation $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ connects two atoms. However, these are unlike atoms and the lattice is therefore *not* body-centered. It is, by elimination, simple cubic. If one wishes, one may think of both ions, the caesium at 0 0 0 and the chlorine at $\frac{1}{2} \frac{1}{2} \frac{1}{2}$, as being

associated with the lattice point at 0 0 0. It is not possible, however, to associate any one caesium ion with any particular chlorine ion and refer to them as a CsCl molecule; the term "molecule" therefore has no real physical significance in such a crystal, and the same is true of most inorganic compounds and alloys.

Close inspection of Fig. 2-18(b) will show that the unit cell of NaCl contains 8 ions, located as follows:

4 Na^+ at 0 0 0, $\frac{1}{2} \frac{1}{2} 0$, $\frac{1}{2} 0 \frac{1}{2}$, and $0 \frac{1}{2} \frac{1}{2}$

4 Cl^- at $\frac{1}{2} \frac{1}{2} \frac{1}{2}$, $0 0 \frac{1}{2}$, $0 \frac{1}{2} 0$, and $\frac{1}{2} 0 0$.

The sodium ions are clearly face-centered, and we note that the face-centering translations ($0 0 0$, $\frac{1}{2} \frac{1}{2} 0$, $\frac{1}{2} 0 \frac{1}{2}$, $0 \frac{1}{2} \frac{1}{2}$), when applied to the chlorine ion at $\frac{1}{2} \frac{1}{2} \frac{1}{2}$, will reproduce all the chlorine-ion positions. The Bravais lattice of NaCl is therefore face-centered cubic. The ion positions, incidentally, may be written in summary form as:

4 Na^+ at 0 0 0 + face-centering translations.

4 Cl^- at $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ + face-centering translations.

Note also that in these, as in all other structures, the operation of any symmetry element possessed by the lattice must bring similar atoms or ions into coincidence. For example, in Fig. 2-18(b), 90° rotation about the 4-fold [010] rotation axis shown brings the chlorine ion at $0 1 \frac{1}{2}$ into coincidence with the chlorine ion at $\frac{1}{2} 1 1$, the sodium ion at $0 1 1$ with the sodium ion at $1 1 1$, etc.

Elements and compounds often have closely similar structures. Figure 2-19 shows the unit cells of diamond and the zinc-blende form of ZnS. Both are face-centered cubic. Diamond has 8 atoms per unit cell, located at

0 0 0 + face-centering translations

$\frac{1}{4} \frac{1}{4} \frac{1}{4}$ + face-centering translations.

The atom positions in zinc blende are identical with these, but the first set of positions is now occupied by one kind of atom (S) and the other by a different kind (Zn).

Note that diamond and a metal like copper have quite dissimilar structures, although both are based on a face-centered cubic Bravais lattice. To distinguish between these two, the terms "diamond cubic" and "face-centered cubic" are usually used. The industrially important semiconductors, silicon and germanium, have the diamond cubic structure.

Instead of referring to a structure by name, such as the "NaCl structure," one can use the designations introduced years ago in *Strukturbericht* [G.1]. These consist of a letter and a number: the letter A indicates an element, B an AB compound, C an AB_2 compound, etc. The structure of copper, for example, is called the A1 structure, α -Fe is A2, zinc is A3, diamond is A4, NaCl is B1, etc. A full list is given by Pearson [G.16, Vol. 1, p. 85].

Some rather complex crystals can be built on a cubic lattice. For example, the ferrites, which are magnetic and are used as memory cores in digital computers, have the formula $\text{MO} \cdot \text{Fe}_2\text{O}_3$, where M is a divalent metal ion like Mn, Ni, Fe, Co, etc. Their structure is related to that of the mineral spinel. The Bravais lattice of the ferrites is face-centered cubic, and the unit cell contains 8 "molecules" or

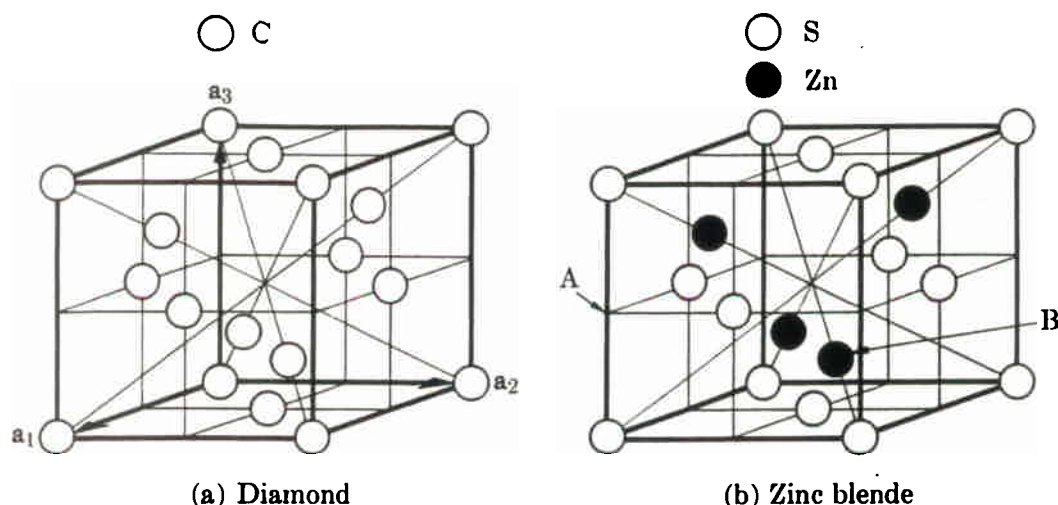


Fig. 2-19 The structures of (a) diamond (common to Si, Ge, and gray Sn) and (b) the zinc-blende form of ZnS (common to HgS, CuI, AlSb, BeSe, etc.).

total of $8 \times 7 = 56$ ions. There are therefore $56/4$ or 14 ions associated with each lattice point.

The number of atoms per unit cell in any crystal is partially dependent on its Bravais lattice. For example, the number of atoms per unit cell in a crystal based on a body-centered lattice must be a multiple of 2, since there must be, for any atom in the cell, a corresponding atom of the same kind at a translation of $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ from the first. The number of atoms per cell in a base-centered lattice must also be a multiple of 2, as a result of the base-centering translations. Similarly, the number of atoms per cell in a face-centered lattice must be a multiple of 4.

The reverse of these propositions is not true. It would be a mistake to assume, for example, that if the number of atoms per cell is a multiple of 4, then the lattice is necessarily face-centered. The unit cell of the intermediate phase AuBe, for example (Fig. 2-20), contains 8 atoms and yet it is based on a simple cubic Bravais lattice. The atoms are located as follows:

4 Au at

$$u u u, (\frac{1}{2} + u) (\frac{1}{2} - u) \bar{u}, \bar{u} (\frac{1}{2} + u) (\frac{1}{2} - u), (\frac{1}{2} - u) \bar{u} (\frac{1}{2} + u),$$

4 Be at

$$w w w, (\frac{1}{2} + w) (\frac{1}{2} - w) \bar{w}, \bar{w} (\frac{1}{2} + w) (\frac{1}{2} - w), (\frac{1}{2} - w) \bar{w} (\frac{1}{2} + w),$$

where $u = 0.100$ and $w = 0.406$, each ± 0.005 . If the parameter u is put equal to zero, the atomic coordinates of the gold atoms become those of a face-centered cubic cell. The structure of AuBe may therefore be regarded as distorted face-centered cubic, in which the presence of the beryllium atoms has forced the gold atoms out of their original positions by a distance $\pm u, \pm u, \pm u$. These translations are all in directions of the form $\langle 111 \rangle$, i.e., parallel to body diagonals of the cube, and are shown as dotted lines in Fig. 2-20.

It should now be apparent that the term "simple," when applied to a Bravais lattice, is used in a very special, technical sense and that some very complex structures can be built up on a "simple" lattice. In fact, they may contain more than a hundred atoms per unit cell. The only workable definition of a simple

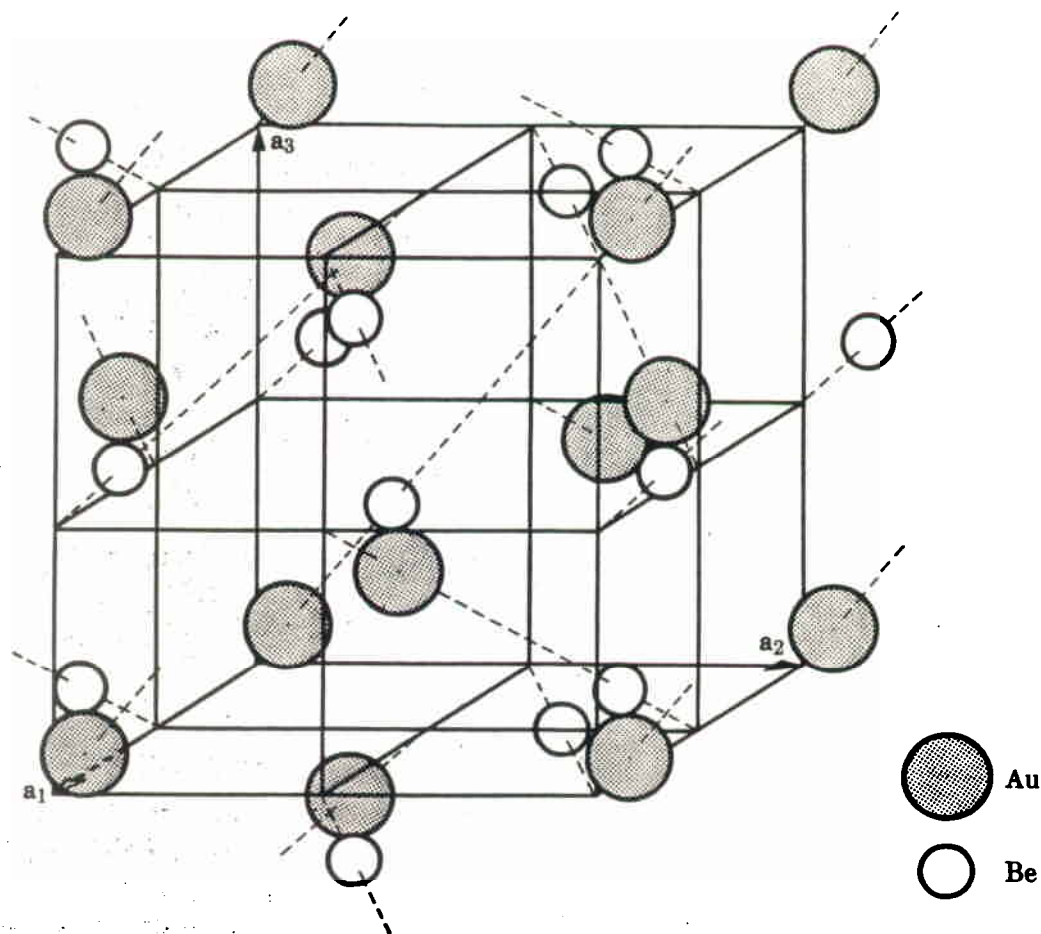


Fig. 2-20 The structure of AuBe, shared by FeSi, NiSi, CoSi, MnSi, etc. It is known as the FeSi structure [2.2].

lattice is a negative one: a given lattice is simple if it is neither body-, base-, nor face-centered; these latter possibilities can be ruled out by showing that the set of atomic positions does not contain the body-, base-, or face-centering translations. There is no rule governing the allowable number of atoms per cell in a simple lattice: this number may take on any one of the values 1, 2, 3, 4, 5, etc., although not in every crystal system and not every higher integer is permitted. Incidentally, not every theoretical possibility known to mathematical crystallography is realized in nature; for example, no known element crystallizes with a simple hexagonal lattice containing one atom per unit cell.

There is one other way of arranging unlike atoms on a point lattice besides those considered so far and that is exemplified by the structure of *solid solutions*. These solutions are of two types, substitutional and interstitial; in the former, solute atoms substitute for, or replace, solvent atoms on the lattice of the solvent, while in the latter, solute atoms fit into the interstices of the solvent lattice. The interesting feature of these structures is that the solute atoms are distributed more or less at random. For example, consider a 10 atomic percent solution of molybdenum in chromium, which has a BCC structure. The molybdenum atoms can occupy either the corner or body-centered positions of the cube in a random, irregular manner, and a small portion of the crystal might have the appearance of Fig. 2-21(a). Five adjoining unit cells are shown there, with a total of 29 atoms,

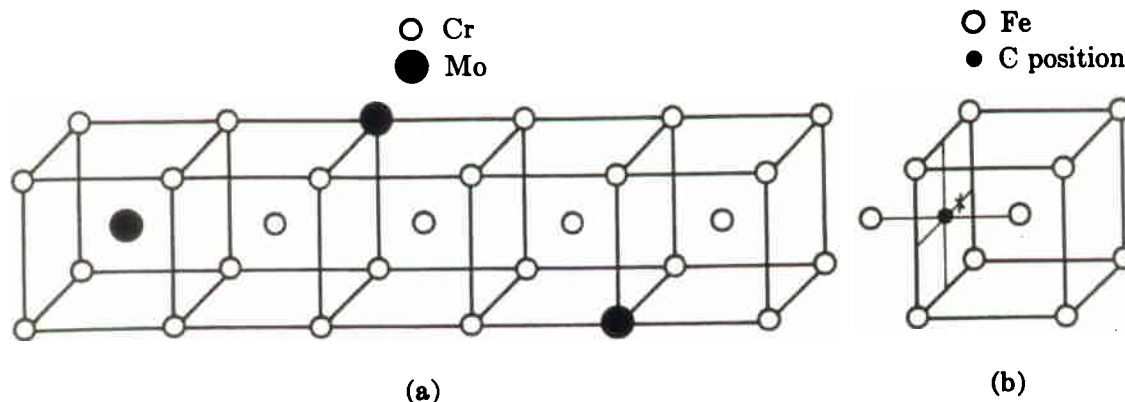


Fig. 2-21 Structure of solid solutions: (a) Mo in Cr (substitutional); (b) C in α -Fe (interstitial).

3 of which are molybdenum. This section of the crystal therefore contains somewhat more than 10 atomic percent molybdenum, but the next five cells would probably contain somewhat less. Such a structure does not obey the ordinary rules of crystallography: for example, the right-hand cell of the group shown does not have cubic symmetry, and one finds throughout the structure that the translation given by one of the unit cell vectors may begin on an atom of one kind and end on an atom of another kind. All that can be said of this structure is that it is BCC *on the average*, and experimentally we find that it displays the x-ray diffraction effects proper to a BCC lattice. This is not surprising since the x-ray beam used to examine the crystal is so large compared to the size of a unit cell that it observes, so to speak, millions of unit cells at the same time and so obtains only an average "picture" of the structure.

The above remarks apply equally well to interstitial solid solutions. These form whenever the solute atom is small enough to fit into the solvent lattice without causing too much distortion. Ferrite, the solid solution of carbon in α -iron, is a good example.* In the unit cell shown in Fig. 2-21(b), there are two kinds of "holes" in the lattice: one at $\frac{1}{2} 0 \frac{1}{2}$ (marked \bullet) and equivalent positions in the centers of the cube faces and edges, and one at $\frac{1}{4} 0 \frac{1}{4}$ (marked \times) and equivalent positions. All the evidence at hand points to the fact that the carbon atoms in ferrite are located in the holes at $\frac{1}{2} 0 \frac{1}{2}$ and equivalent positions. On the average, however, no more than about 1 of these positions in 500 unit cells is occupied, since the maximum solubility of carbon in ferrite is only about 0.1 atomic percent.

Still another type of structure worth noting is that of *ordered solid solutions*. As described above, a typical substitutional solid solution has solute atoms distributed more or less at random on the lattice points of the solvent.† On the other hand, there are solutions in which this is true only at elevated temperatures; when cooled to lower temperatures, the solute atoms take up an orderly, periodic

* Note the double meaning of the word *ferrite*: (1) metallurgical, for the metallic solid solution mentioned above, and (2) mineralogical, for the oxide $\text{MO} \cdot \text{Fe}_2\text{O}_3$ previously described.

† Of course, when the solution becomes concentrated, there is no real distinction between "solvent" and "solute." There is only one lattice, with two or more kinds of atoms distributed on it.

arrangement while still remaining on the lattice points of the solvent. The solid solution is then said to be *ordered* and to possess a *superlattice*. The alloy AuCu_3 is a classic example: at high temperatures the copper and gold atoms are located more or less at random on face-centered cubic lattice sites, while at low temperature the gold atoms occupy only the cube corner positions and the copper atoms only the face-centered positions. In its temperature range of stability then, an ordered solid solution resembles a chemical compound, with atoms of one kind on one set of lattice sites and atoms of a different kind on another set. But an ordered solid solution is a “half-hearted compound” because, when heated, it disorders before it melts; a real compound, like NaCl , remains ordered right up to the melting point. Crystallographically, the structures of the disordered and ordered solid solutions are quite different; disordered AuCu_3 is, on the average, face-centered cubic while the ordered form is simple cubic. Such structures will be discussed more fully in Chap. 13.

2-8 ATOM SIZES AND COORDINATION

When two or more unlike atoms unite to form a chemical compound, intermediate phase, or solid solution, the kind of structure formed is dependent, in part, on the relative sizes of the atoms involved. But what is meant by the size of an atom? To regard an atom as something like a billiard ball with a sharply defined bounding surface is surely an oversimplification, since we know that the electron density decreases gradually at the “surface” of the atom and that there is a small but finite probability of finding an electron at quite large distances from the nucleus. And yet the only practical way we have of defining atomic size lies in considering a crystal as a collection of rigid spheres in contact. The size of an atom, then, is given by the distance of closest approach of atom centers in a crystal of the element, and this distance can be calculated from the lattice parameters.

For example, the lattice parameter a of α -iron is 2.87 \AA , and in a BCC lattice the atoms are in contact only along the diagonals of the unit cube. The diameter of an iron atom is therefore equal to one half the length of the cube diagonal, or $(\sqrt{3}/2)a = 2.48 \text{ \AA}$. The following formulas give the distance of closest approach in the three common metal structures:

$$\begin{aligned} \text{BCC} &= \frac{\sqrt{3}}{2} a, \\ \text{FCC} &= \frac{\sqrt{2}}{2} a, \\ \text{HCP} &= a \quad (\text{between atoms in basal plane}), \\ &= \sqrt{\frac{a^2}{3} + \frac{c^2}{4}} \quad (\text{between atom in basal plane and neighbors above or below}). \end{aligned} \tag{2-7}$$

Values of the distance of closest approach, together with the crystal structures and lattice parameters of the elements, are tabulated in Appendix 5.

To a first approximation, the size of an atom is a constant. In other words, an iron atom has about the same size whether it occurs in pure iron, an intermediate phase, or a solid solution. This is a very useful fact to remember when investigating unknown crystal structures, for it enables us to predict roughly how large a hole is necessary in a proposed structure to accommodate a given atom. More precisely, it is known that the size of an atom has a slight dependence on its *coordination number*, which is the number of nearest neighbors of the given atom and which depends on crystal structure. The coordination number of an atom in the FCC or HCP structures is 12, in BCC 8, and diamond cubic 4. The smaller the coordination number, the smaller the volume occupied by a given atom, and the approximate amount of contraction to be expected with decrease in coordination number is found to be:

Change in coordination	Size contraction, percent
12 \rightarrow 8	3
12 \rightarrow 6	4
12 \rightarrow 4	12

This means, for example, that the diameter of an iron atom is greater if the iron is dissolved in FCC copper than if it exists in a crystal of BCC α -iron or is dissolved in BCC vanadium. If it were dissolved in copper, its diameter would be approximately $2.48/0.97$, or 2.56 \AA .

The size of an atom in a crystal also depends on whether its binding is ionic, covalent, metallic, or van der Waals, and on its state of ionization. The more electrons are removed from a neutral atom the smaller it becomes, as shown strikingly for iron, whose atoms and ions Fe , Fe^{++} , Fe^{+++} have diameters of 2.48, 1.66, and 1.34 \AA , respectively.

The spatial arrangement of atoms about a given point is often described by words such as *octahedral* and *tetrahedral*. For example, in the NaCl structure of Fig. 2-18(b) the central Cl^- ion at $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ is said to be octahedrally surrounded by Na^+ ions, because the six Na^+ ions in the face-centered positions lie on the corners of an octahedron, a solid bounded by eight triangular sides. In the zinc blende structure of Fig. 2-19(b) the empty position marked *A* is octahedrally surrounded by sulphur atoms, of which only four are in the cell shown, and would be referred to as an octahedral hole in the structure. This group of atoms is shown separately in Fig. 2-22. In the same structure the Zn atom at $\frac{3}{4} \frac{3}{4} \frac{1}{4}$, marked *B* in Fig. 2-19(b), is surrounded by four S atoms at the corners of a tetrahedron, a solid bounded by four triangular sides (Fig. 2-22). In fact, all four of the Zn atoms in the unit cell have tetrahedral S surroundings. Also in the ZnS structure the reader can demonstrate, by sketching three cells adjacent to the one shown, that the hole at *A* is tetrahedrally surrounded by Zn atoms. Thus, the hole at *A* has both octahedral (S) and tetrahedral (Zn) surroundings, an unusual circumstance.

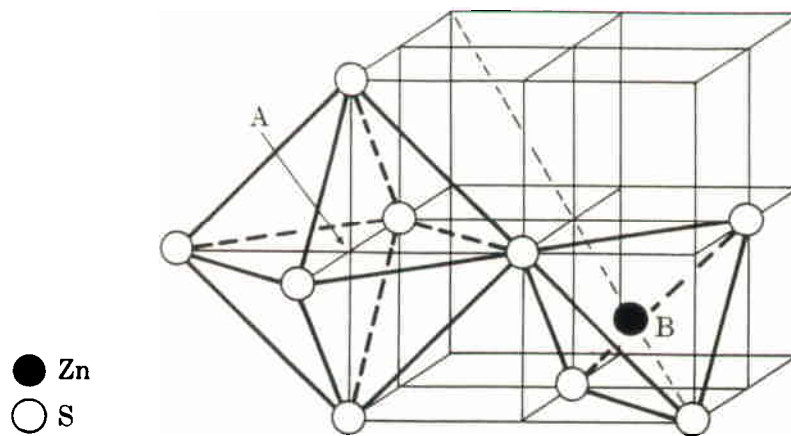


Fig. 2-22 Portion of the zinc blende structure. Compare Fig. 2-19(b). The hole at *A* has octahedral surroundings. The Zn atom at *B* has tetrahedral surroundings.

2-9 CRYSTAL SHAPE

We have said nothing so far about the shape of crystals, preferring to concentrate instead on their interior structure. However, the shape of crystals is, to the layman, perhaps their most characteristic property, and nearly everyone is familiar with the beautifully developed flat faces exhibited by natural minerals or crystals artificially grown from a supersaturated salt solution. In fact, it was with a study of these faces and the angles between them that the science of crystallography began.

Nevertheless, the shape of crystals is really a secondary characteristic, since it depends on, and is a consequence of, the interior arrangement of atoms. Sometimes the external shape of a crystal is rather obviously related to its smallest building block, the unit cell, as in the little cubical grains of ordinary table salt (NaCl has a cubic lattice) or the six-sided prisms of natural quartz crystals (hexagonal lattice). In many other cases, however, the crystal and its unit cell have quite different shapes; gold, for example, has a cubic lattice, but natural gold crystals are octahedral in form, i.e., bounded by eight planes of the form $\{111\}$.

An important fact about crystal faces was known long before there was any knowledge of crystal interiors. It is expressed as the *law of rational indices*, which states that the indices of naturally developed crystal faces are always composed of small whole numbers, rarely exceeding 3 or 4. Thus, faces of the form $\{100\}$, $\{111\}$, $\{1\bar{1}00\}$, $\{210\}$, etc., are observed but not such faces as $\{510\}$, $\{719\}$, etc. We know today that planes of low indices have the largest density of lattice points, and it is a law of crystal growth that such planes develop at the expense of planes with high indices and few lattice points.

To a metallurgist, however, crystals with well-developed faces are in the category of things heard of but rarely seen. They occur occasionally on the free surface of castings, in some electrodeposits, or under other conditions of no external constraint. To a metallurgist, a crystal is most usually a "grain," seen through a microscope in the company of many other grains on a polished section. If he has an isolated single crystal, it will have been artificially grown either from the melt, and thus have the shape of the crucible in which it solidified, or by re-

crystallization, and thus have the shape of the starting material, whether sheet, rod, or wire.

The shapes of the grains in a polycrystalline mass of metal are the result of several kinds of forces, all of which are strong enough to counteract the natural tendency of each grain to grow with well-developed flat faces. The result is a grain roughly polygonal in shape with no obvious aspect of crystallinity. Nevertheless, that grain is a crystal and just as "crystalline" as, for example, a well-developed prism of natural quartz, since the essence of crystallinity is a periodicity of inner atomic arrangement and not any regularity of outward form.

2-10 TWINNED CRYSTALS

Some crystals have two parts symmetrically related to one another. These, called twinned crystals, are fairly common both in minerals and in metals and alloys. For a detailed discussion of twinning, see Kelly and Groves [G.33] and Barrett and Massalski [G.25].

The relationship between the two parts of a twinned crystal is described by the symmetry operation which will bring one part into coincidence with the other or with an extension of the other. Two main kinds of twinning are distinguished, depending on whether the symmetry operation is 180° rotation about an axis, called the twin axis, or reflection across a plane, called the twin plane. The plane on which the two parts of a twinned crystal are united is called the composition plane. In the case of a reflection twin, the composition plane may or may not coincide with the twin plane.

Of most interest to metallurgists, who deal mainly with FCC, BCC, and HCP structures, are the following kinds of twins:

1. Annealing twins, such as occur in FCC metals and alloys (Cu, Ni, α -brass, Al, etc.), which have been cold-worked and then annealed to cause recrystallization.
2. Deformation twins, such as occur in deformed HCP metals (Zn, Mg, Be, etc.) and BCC metals (α -Fe, W, etc.).

Annealing Twins

Annealing twins in FCC metals are rotation twins, in which the two parts are related by a 180° rotation about a twin axis of the form $\langle 111 \rangle$. Because of the high symmetry of the cubic lattice, this orientation relationship is also given by a 60° rotation about the twin axis or by reflection across the $\{111\}$ plane normal to the twin axis. In other words, FCC annealing twins may also be classified as reflection twins. The twin plane is also the composition plane.

Occasionally, annealing twins appear under the microscope as in Fig. 2-23(a), with one part of a grain (B) twinned with respect to the other part (A). The two parts are in contact on the composition plane (111) which makes a straight-line trace on the plane of polish. More common, however, is the kind shown in Fig. 2-23(b). The grain shown consists of three parts: two parts (A_1 and A_2) of identical orientation separated by a third part (B) which is twinned with respect to A_1 and A_2 . B is known as a twin band.