

**TOPIC 1: CRYSTALLOGRAPHY**PRIMARY READING ASSIGNMENT

"The Elements of Crystallography", from *The Physics of Solids*, F.C. Brown.

SUPPLEMENTARY REFERENCE

"Materials Properties and Crystal Lattices", from *Solid State Physics*, J.P. McKelvey  
"The Geometry of Crystals", from *Elements of X-ray Diffraction*, B.D. Cullity

LECTURE PROGRAM

1. External Form and the Structure of Crystals
  - a. Overview
  - b. Lattice point, space lattice / Bravais lattice
  - c. Basis, crystal structure
2. Translation Vectors and Periodicity
  - a. Elementary translationa vectors
  - b. Translational symmetry
3. The Concept of a Unit Cell
  - a. Unit cell
  - b. Primitive cell
  - c. Wigner-Seitz cell
4. Point Group Symmetries
  - a. Point group
  - b. Inversion
  - c. Reflection
  - d. Rotation
  - e. Rotation-Inversion
  - f. Implied symmetry
  - g. Excluded symmetry
5. The Fourteen Bravais Lattices
6. Miller Indices
7. Stereographic Projections
8. The Thirty-Two Crystallographic Point Groups
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9. Point-Group Symmetry and Physical Properties
  - a. Neuman principle
  - b. Pyroelectricity
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  - d. Electrical conductivity
10. Space Groups and Notations
  - a. Screw axis
  - b. Glide plane
11. Crystal Structures
  - a. Simple cubic
  - b. CsCl
  - c. Body-centered cubic
  - d. Face-centered cubic
  - e. Diamond lattice
  - f. Zinc blende
  - g. Hexagonal close packed

# **CHAPTER 2**

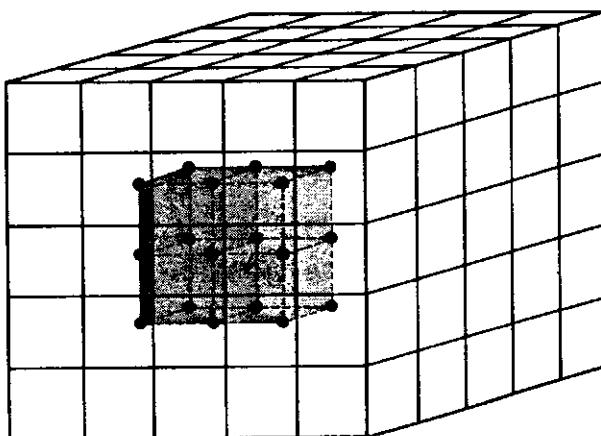
## **THE ELEMENTS OF CRYSTALLOGRAPHY**

### **2-1 EXTERNAL FORM AND THE STRUCTURE OF CRYSTALS**

An early basis for understanding solids was established by the classification of rocks and minerals. Most rock specimens appear to be amorphous in form, but those which are obviously crystalline have always held great fascination [1]. The science of crystallography developed with the study of the external form and habit of naturally occurring crystals. In this study crystals were not considered as a lattice structure of atoms, as we view them today, but rather as solids bounded by a series of faces [2]. The investigation of the angles between these faces dates back to the seventeenth century and shows that crystals fall into 32 different classes. These classes can be identified with the 32 different point groups, which characterize the symmetry at a point in the lattice. The relationship between the external form of crystals and point-group symmetry is beautifully discussed in the book by F. C. Phillips [3].

Under certain naturally occurring conditions and also in the laboratory [4], some materials (sodium chloride, for example) crystallize into nearly perfect cubes. Now it is easy to imagine that such an external form arises from the stacking of a myriad tiny cubes somewhat like those shown in Fig. 2-1. A better procedure, however, is to develop a structural unit with atoms at the center of gravity of each cubelet as shown by the dots connected by dashed lines in Fig. 2-1. This bears a closer resemblance to the results of x-ray diffraction experiments which tell us that atoms and their associated electrons are arranged about the points of a *lattice*.

In Fig. 2-1 we imagine identical atoms placed at each *lattice point*, and we define a simple cubic cell for the lattice by drawing lines connecting eight such atoms. Each atom at the corners of this cell is shared by eight similar cells; therefore such a cell is primitive in that only one atom need be involved. We could also show this by displacing the point lattice slightly with respect to the atoms. Such a cell is a *unit cell*, since we only need to describe one cell and its contents to define the entire crystal structure. Identical unit cells can be packed together to fill all of space to form the entire crystal. Actually, the simple cubic structure of Fig. 2-1 is highly unusual even for elemental solids. The sodium chloride structure is not quite this simple since two different ions are involved as shown in Fig. 1-1. More will be said about unit cells in Section 2-3.



**FIGURE 2-1.** Showing the way in which an external cubic form can arise out of the stacking of tiny cublets. The dotted lines show a lattice structure formed by placing points (atoms) at the center of each cube.

At this point we would like to emphasize the difference between a *Bravais* or *space lattice* and a crystal structure. A *Bravais* lattice is simply a lattice of points in space formed by repeating units, for example, the cubic lattice which can be seen in Fig. 2-1 if one replaces the atoms by points. There are only 14 different Bravais lattices in all; the development of these space lattices will be described in Section 2-5. A Bravais lattice is just a discrete set of points in space which looks the same when viewed from any one of its points as when viewed from any other lattice point.

A crystal structure is formed by placing what is known as a *basis* down on each point of a Bravais lattice. A basis might consist of a single atom (or ion), a group of atoms, or a molecule. An identical arrangement and orientation of the basis is to be found at each lattice point. In this

way, the crystal is formed by repeating the basis in space as prescribed by the particular Bravais or space lattice involved. There are many different crystal structures and a few of these will be discussed in Section 2-12.

## 2-2 TRANSLATION VECTORS AND PERIODICITY

The most important general feature of a Bravais lattice is its translational symmetry or translational periodicity. An oblique Bravais lattice (triclinic *P*) is shown in Fig. 2-2. Three vectors **a**, **b**, and **c** are shown which correspond to elementary translations along three different directions. These vectors are the fundamental translation vectors and are picked as follows:

- a** = shortest period in the lattice (or one of several equally short),
- b** = shortest period not parallel to **a**,
- c** = shortest period not coplanar to **a** and **b**.

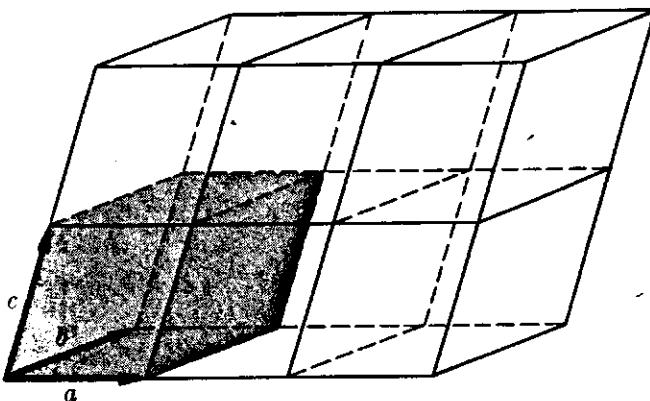


FIGURE 2-2. An oblique Bravais lattice with elementary translation vectors **a**, **b**, and **c**.

Translational symmetry or periodicity is made clear as follows: Let  $\mathbf{r}$  be any position in the lattice. Consider another position  $\mathbf{r}'$  which is obtained from  $\mathbf{r}$  by the following equation, where  $n_1$ ,  $n_2$ , and  $n_3$  are integers.

$$\mathbf{r}' = \mathbf{r} + n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}. \quad (2-1)$$

Translational symmetry requires that the lattice arrangement appear the same at  $\mathbf{r}'$  as at  $\mathbf{r}$ . The translation operation in this case consists of adding the vector

$$\mathbf{T} = n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c} \quad (2-2)$$

to the vector  $\mathbf{r}$ . A shorthand way of writing Eq. (2-1) would be in terms of an operator as follows

$$T_{n_1 n_2 n_3} \mathbf{r} = \mathbf{r}', \quad (2-3)$$

where the subscripts designate particular integers  $n_1, n_2, n_3$ . The totality of operations for all values of  $n_1, n_2$ , and  $n_3$  is known as the translation group for the crystal. The translation group is a part of the *space group* which includes both translation and rotation operations.

Translational symmetry requires that the lattice must be exactly the same in the vicinity of the point  $\mathbf{r}'$  as in the vicinity of  $\mathbf{r}$ . Strictly speaking, this requirement can be met only for an infinite crystal or near the center of a very large crystal. There is, however, a way of getting around this difficulty for a crystal containing a large but finite number of lattice points. If the crystal is big enough, the nature of the boundary conditions is irrelevant to all discussions of bulk physical properties. We therefore choose the simplest conditions called periodic boundary conditions in which one requires that the crystal be bent back upon itself so to speak. Take a crystal of size  $N_1\mathbf{a}$  by  $N_2\mathbf{b}$  by  $N_3\mathbf{c}$  where  $N_1, N_2$ , and  $N_3$  are large numbers. We then require that the three translations  $N_1\mathbf{a}, N_2\mathbf{b}, N_3\mathbf{c}$  affect no change in any physical quantity, i.e., they are equal to zero translation as follows:

$$T_{N_1 00} = T_{0N_2 0} = T_{00N_3} = T_{000}. \quad (2-4)$$

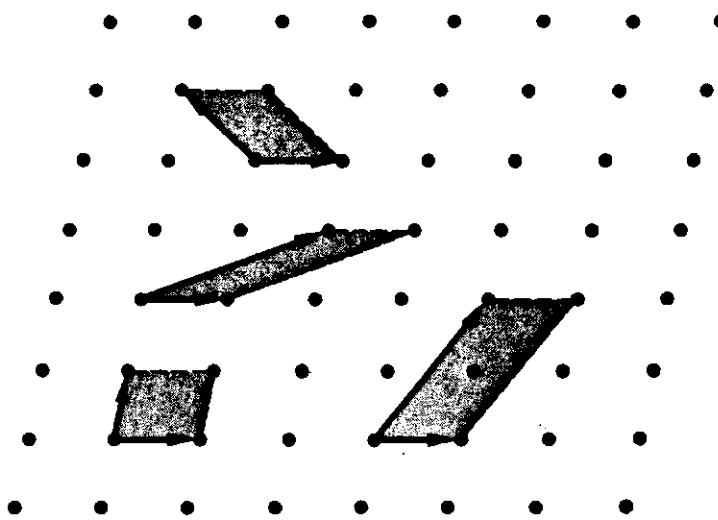
Such conditions are an artifact particularly useful in connection with the theory of lattice vibrations as well as in the behavior of electrons in a crystal.

In the above discussion translational periodicity was described in terms of the vectors  $\mathbf{a}, \mathbf{b}$ , and  $\mathbf{c}$  that define the edges of the primitive cell. That is, the lattice itself can be generated by translating the primitive cell so that all space is covered. As mentioned above, the primitive cell of a Bravais lattice is a unit cell which contains at most one lattice point. The idea of a unit cell will be clarified in the next section.

### 2-3 THE CONCEPT OF A UNIT CELL

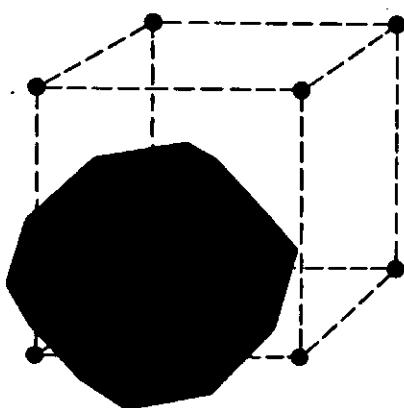
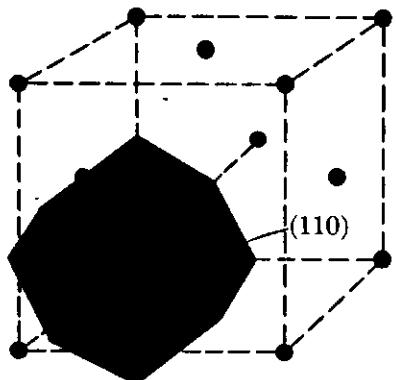
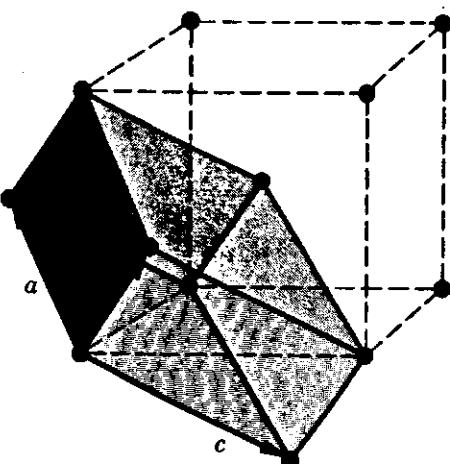
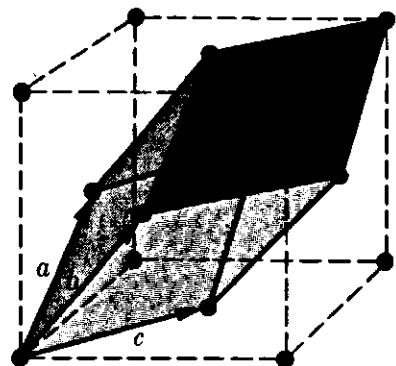
A unit cell is evidently a small unit of the crystal which, when repeated, develops the entire crystal pattern. The shape of the unit cell must be chosen so that identical cells can be packed together to fill the entire volume of the crystal. One need only specify the nature of the unit cell, its shape, dimensions, and constitution, to define the crystal as a whole.

The choice of the unit cell is to a certain extent arbitrary. For example, it need not always be primitive, and also it can take on different shapes. This is illustrated in Fig. 2-3 for an oblique lattice in two dimensions. Three different primitive cells are shown, together with one non-primitive cell. The primitive cells have atoms at their corners only, or they may be drawn displaced slightly so as to enclose one atom. All primitive cells will have the same area. Our figure shows a plane two-dimensional net, but similar ideas can be carried over to three dimensions.



**FIGURE 2-3.** Showing three primitive cells and one nonprimitive cell (lower right) for an oblique lattice in two dimensions.

The unit cell is often chosen so as to reveal by the form of the cell itself the symmetry of the lattice. This sometimes results in a larger cell which is not primitive. Three different choices of unit cells for the face-centered cubic and the body-centered cubic lattices (refer to Section 2-12) are shown in Fig. 2-4. The conventional cubic unit cells are shown by dotted lines, whereas the rhombohedral primitive cells are indicated by the fundamental translation vectors  $\mathbf{a}$ ,  $\mathbf{b}$ , and  $\mathbf{c}$  and the solid lines. The so-called Wigner-Seitz cells are also shown in Fig. 2-4, and these are polyhedra constructed about each atom by drawing planes which are the perpendicular bisectors of the lines between nearest neighbors. A little thought will show that these polyhedra can be packed together so as to fill all space and each clearly reveals the cubic symmetry of a lattice point. The symmetry at a point in the lattice is most important, both in relation to the configuration of forces on atoms in the crystal and also in regard to the physical properties of crystals. The nature of point-group symmetry is described in the next section.



(a) Face-centered cubic

(b) Body-centered cubic

**FIGURE 2-4.** Various unit cells for the face-centered and body-centered cubic Bravais lattices. The conventional cubic cells are indicated above by dotted lines, the rhombohedral cells by the vectors  $a$ ,  $b$ ,  $c$  and solid lines. The Wigner-Seitz unit cells for each lattice are shown in the lower part of the figure.

#### 2-4 ROTATIONAL SYMMETRY IN CRYSTALS

Group theory can be widely applied to problems in solid state and quantum physics [5, 6]. We will not study group theory here but, realizing its importance, familiarize ourselves with some of its consequences and terminology, especially in connection with crystallographic point groups. A point group is a collection of symmetry operations, such as rotations about an axis which conceivably apply at a point in space, that is, operations which leave one point fixed. These symmetry operations might be applied to a molecule, to a crystal of some external form, or to the region surrounding a point in a lattice structure. Translation is not involved since it does not leave one point fixed. Point-group symmetry

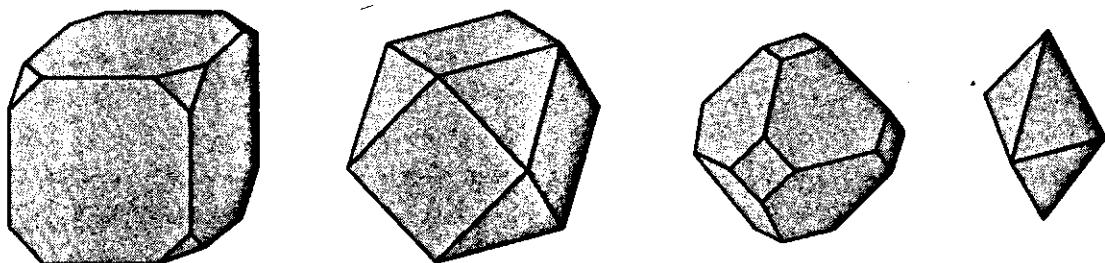
is sometimes considered to apply at the position of an atom in the lattice and sometimes at a point between atoms. Let us first consider the various possible symmetry elements and then the 32 crystallographic point groups that consist of combinations of these elements.

The various symmetry elements under consideration are: (a) inversion center, (b) reflection plane, (c) rotation axis, and (d) rotation-inversion axis, and we will discuss each in order.

(a) *Inversion center*: indicated by the symbol  $\bar{1}$ ,  $i$ , or  $S_2$ . The point under consideration is an inversion center if for every arbitrary position  $\mathbf{r}$  ( $\mathbf{r}$  is drawn from the center of inversion), there is another identical position for which

$$\mathbf{r} = -\mathbf{r}. \quad (2-5)$$

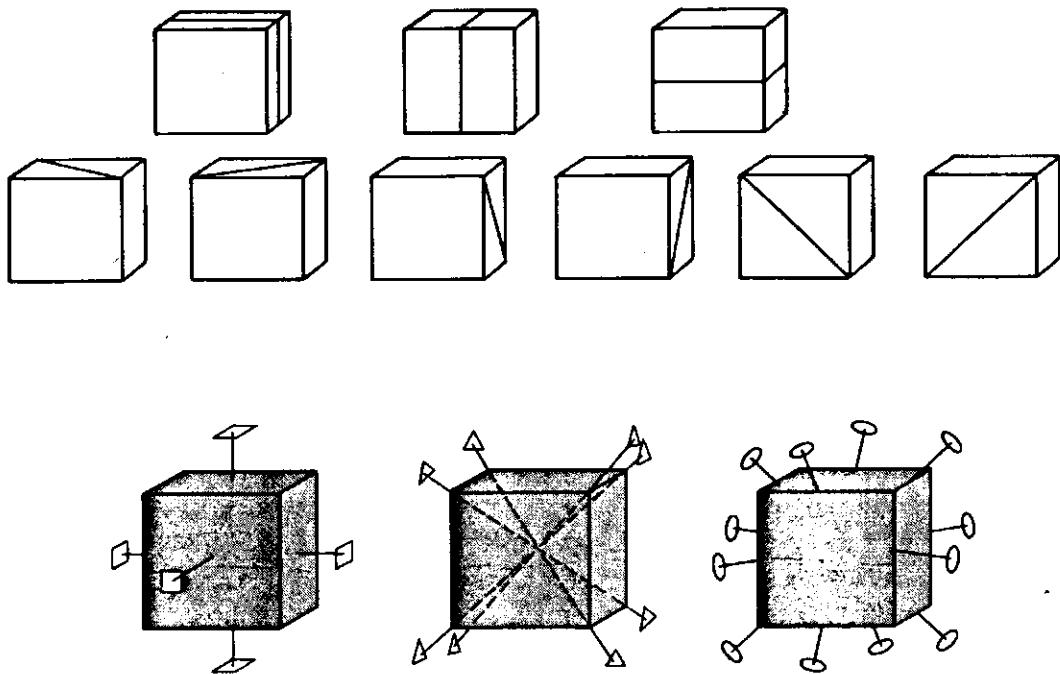
Crystals having planes which occur in pairs have an inversion center, that is, a center of symmetry. For example, the external form of some cubic crystals reveals a center of symmetry. This can be seen for various modifications, where each face has an opposite face parallel to it as shown in Fig. 2-5.



**FIGURE 2-5.** Some modifications of a cube. All are found in the external form of real crystals.

All Bravais lattices have an inversion center, but this is not true of all real crystals or crystal structures. Many important substances lack a center of symmetry, for example, quartz, CdS, ZnO, and others. As a result these substances have characteristic physical properties as discussed in Section 2-9.

(b) *Reflection plane*: indicated by the symbol  $m$  or  $\sigma$ . A reflection plane or plane of mirror symmetry is commonly found passing through lattice points or between lattice points. Mirror planes are also sometimes evident in the external form of crystals. For example, a simple cube has three half-planes of symmetry and six diagonal planes as shown in Fig. 2-6. Points on one side of a plane of symmetry are reflected by identical points on the other side—hence the synonymous terms mirror and reflection plane.



**FIGURE 2-6.** The reflection planes and various axes of rotation symmetry of a cube. The 4-fold axes are indicated by  $\square$ , 3-fold by  $\triangle$ , and 2-fold by  $\circlearrowleft$ .

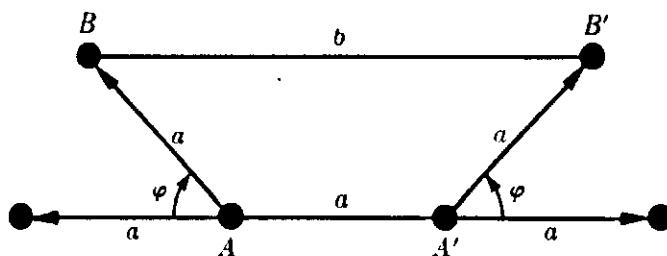
(c) *Rotation axis:* indicated by 1, 2, 3, 4, 6, or  $C_n$ . An  $n$ -fold axis of rotational symmetry exists, if the crystal, upon rotation about this axis, assumes a congruent position  $n$  times per revolution, i.e., each time by rotation through an angle  $360^\circ/n$ . The only rotations consistent with translational symmetry are  $n = 1, 2, 3, 4, 6$ . This will be discussed below. A simple cube has 3-tetrad, 4-triad, and 6-diad axes of rotation as may be seen in Fig. 2-6. These same symmetry elements are to be found in the various modifications of a cube including the octohedral one shown in Fig. 2-5. The triad axes are a distinguishing feature of the cubic system.

(d) *Rotation-inversion axis:* indicated by  $\bar{1}, \bar{2}, \bar{3}, \bar{4}$ , or  $\bar{6}$ . By this we mean a combination operation. A crystal has a rotation-inversion axis, if it is brought into coincidence by a rotation followed by an inversion across a center. The possible operations are

$$\bar{1}, \bar{2}, \bar{3}, \bar{4}, \text{ or } \bar{6},$$

where  $\bar{1}$  is our previously defined inversion center. Note that the rotation inversion element  $\bar{2}$  is the same as reflection in a plane to which the 2-fold axis is perpendicular. Therefore  $\bar{2} = m$ .

Let us return to the point which was made earlier that only 1-, 2-, 3-, 4-, and 6-fold rotation axes are permitted in the case of a Bravais lattice. Simple considerations show that 5- and 7-fold rotation axes are not allowed. We follow an argument given by Buerger [7]. Consider the points  $A$  and  $A'$  of a Bravais lattice located a repeat distance  $a$  apart,



**FIGURE 2-7.** Construction to show the rotations consistent with translational invariance.

as shown in Fig. 2-7. Other lattice points are also shown, for example, those in line with  $A$  and  $A'$  as well as  $B$  and  $B'$ , each a lattice distance  $a$  from  $A$  and  $A'$ , respectively. If an  $n$ -fold rotation axis passes through  $A$  and  $A'$ , the points  $B$  and  $B'$  can be obtained by rotating through the angle  $\varphi = 2\pi/n$  clockwise and counterclockwise as shown. The line  $BB' = b$  must be parallel to the line  $AA'$  and equal in length to some multiple of  $AA' = a$ , that is,  $b = ja$ , where  $j$  is an integer. This last statement must apply in order that the distance  $b$  is a lattice translation distance. A glance at Fig. 2-7 shows that

$$b = a + 2a \cos \varphi = ja. \quad (2-6)$$

This can be rearranged and written in terms of another integer  $i$  as follows

$$\cos \varphi = \frac{j - 1}{2} = \frac{i}{2}. \quad (2-7)$$

The permitted values of  $i$  are found from Eq. (2-7) and given in Table 2-1. Only certain rotations and therefore rotation-inversion operations are permitted. For example, 5-, 7-, and 8-fold axes are incompatible with a continued network of points. The 1-, 2-, 3-, 4-, and 6-fold symmetries are compatible but they may require the net to have a special shape.

**TABLE 2-1.** The Rotation Angle  $\varphi$  and Values of  $n = 2\pi/\varphi$  Permitted by Translational Periodicity, the  $i$  Are Integers as Shown and  $b$  Is a Multiple of a Lattice Distance  $a$

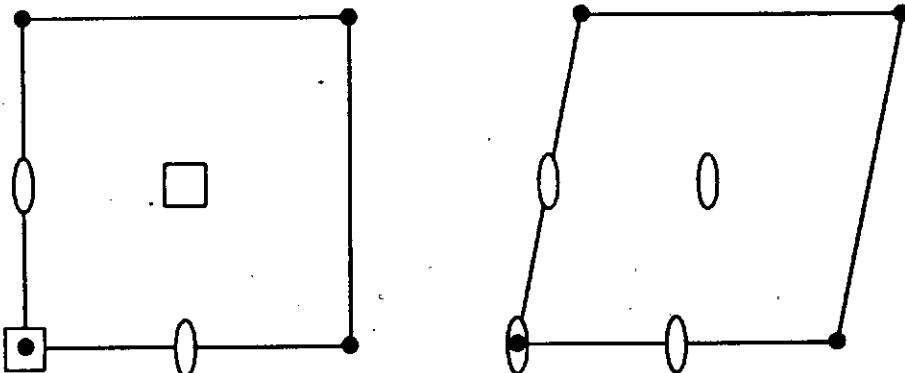
| $i$ | $\cos \varphi$ | $\varphi$ | $n = 2\pi/\varphi$ | $b$  |
|-----|----------------|-----------|--------------------|------|
| -2  | -1             | $\pi$     | 2                  | $-a$ |
| -1  | $-\frac{1}{2}$ | $2\pi/3$  | 3                  | 0    |
| 0   | 0              | $\pi/2$   | 4                  | $a$  |
| 1   | $\frac{1}{2}$  | $\pi/3$   | 6                  | $2a$ |
| 2   | 1              | 0         | $= 1$              | $3a$ |

For example, 4-fold axes require a square net, 3-fold and 6-fold require a network of nested equilateral triangles.

## 2-5 THE FOURTEEN BRAVAIS LATTICES

In the last section we showed for a plane net that only certain rotations, 1-, 2-, 3-, 4-, and 6-fold, are consistent with translational symmetry. The same result holds for a network of points in space, that is, for a Bravais lattice. After all, a lattice in space can just be described as a stack of plane networks—lattice planes uniformly repeated. These lattice planes might be the obvious more densely packed and widely spaced principal planes or the less densely packed but closely spaced planes of a crystal.

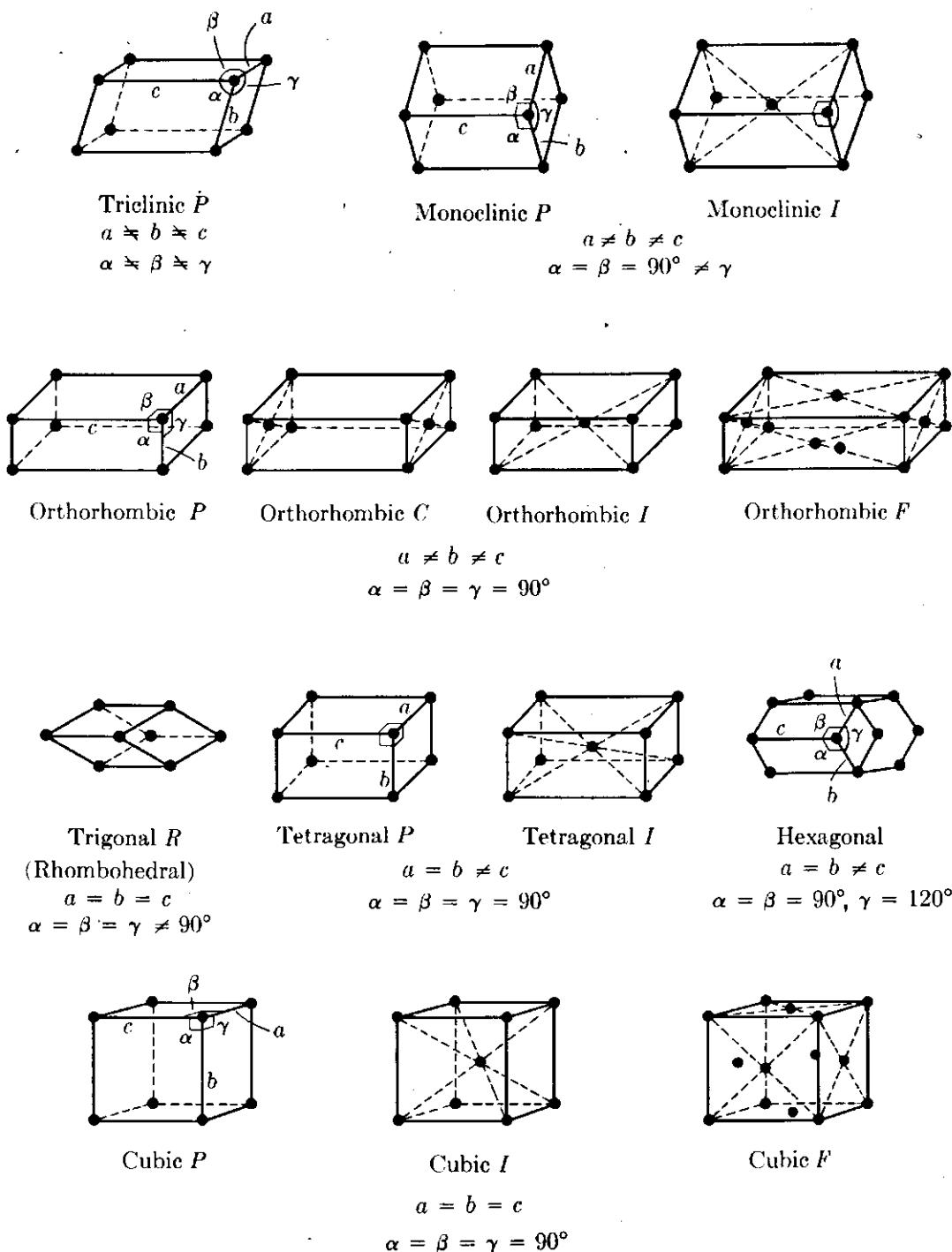
The permitted rotation symmetries are most important in that they form the starting point for developing and classifying the various space lattices. First consider a two-dimensional square net as shown in Fig. 2-8a. This is the plane net required by a 4-fold rotation axis which must at least pass through each lattice point. The square net also has a 4-fold axis at the center of each cell as indicated in Fig. 2-8a. In addition the square net has two 2-fold axes at the points  $\frac{1}{2}, 0$  and  $0, \frac{1}{2}$  as shown. Thus, there are four nonequivalent rotation axes for this plane net. If, by distortion, we form an oblique lattice the 2-diad and 2-tetrad axes of the square net become four nonequivalent 2-fold axes as shown in Fig. 2-8a.



**FIGURE 2-8.** The square net has 4 nonequivalent axes of symmetry. The 4-fold axes become 2-fold upon distortion to form the oblique net shown in b.

All plane nets have at least a 2-fold axis. However, this 2-fold axis is lost if we form a three-dimensional lattice by repeating the net of Fig. 2-8b by displacing in a direction which makes an angle  $\alpha \neq 90^\circ$  with

respect to the plane of the page. This gives rise to the primitive triclinic *P* space lattice shown in Fig. 2-9. The triclinic Bravais lattice does have an inversion center  $\bar{1}$ , as do all Bravais lattices. However, if we place an asymmetrical basis on the points of such a lattice to form a triclinic crystal structure, the symmetry becomes 1 and only translational symmetry prevails.



**FIGURE 2-9.** Conventional unit cells for the 14 Bravais lattices arranged according to the 7 crystal systems.

If the oblique plane net is displaced in a direction at right angles to the plane, a monoclinic *P* lattice results as shown in Fig. 2-9. The next lattice plane can also be formed by displacing and placing one of the atoms at the position  $\frac{1}{2}$ ,  $\frac{1}{2}$ , which forms the body-centered monoclinic *I* lattice shown in the figure (*I* for Innenzentrierte). Side-centered monoclinic lattices could also be formed with atoms appearing at the positions  $\frac{1}{2}$ , 0 or 0,  $\frac{1}{2}$  in alternate planes, but these can be shown equivalent to the monoclinic *I* lattice [5]. All monoclinic structures have at least a 2-fold axis and the Bravais lattice, which has the highest symmetry of the system, possesses a mirror plane to which the 2-fold axis is perpendicular (symmetry  $2/m$  as explained below).

Four orthorhombic Bravais lattices can be constructed out of rectangular nets. These are either primitive, base-centered *C*, body-centered *I*, or face-centered *F*. They can all be characterized by 2-fold axes at right angles as well as by mirror planes. Notice that the various centered unit cells in Fig. 2-9 contain more than one atom. It is, of course, possible to construct primitive unit cells in each case but these do not so clearly reveal the symmetry.

Since a 4-fold axis requires a square net in three dimensions, this leads to either tetragonal or cubic Bravais lattices as shown in Fig. 2-9. There are only two tetragonal lattices, primitive *P* and body-centered *I*. One can construct a base-centered tetragonal structure whose base is of side  $a$ , but it can also be thought of as a tetragonal *P* lattice with a side  $2^{1/2} a/2$ . Similarly a face-centered tetragonal lattice with base of side  $a$  becomes a body-centered lattice of side  $2^{1/2} a/2$ .

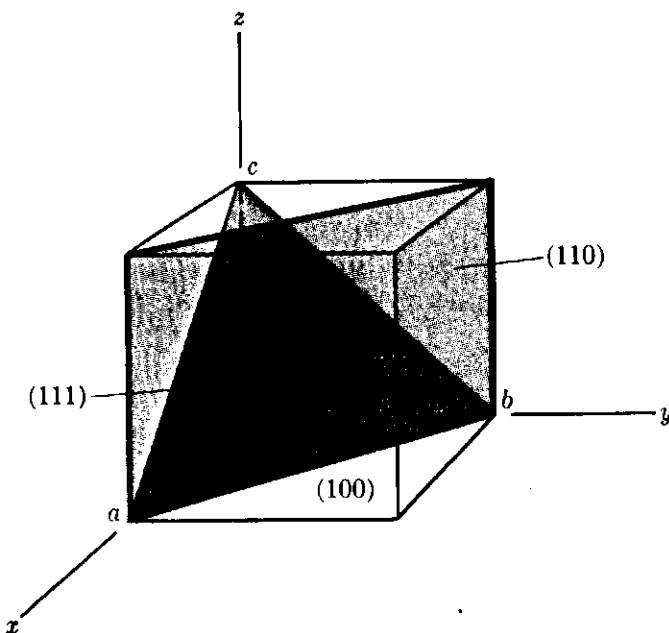
The symmetries  $n = 3$  and  $n = 6$  require a two-dimensional network of equilateral triangles which results in the hexagonal-based prism for the hexagonal system shown in Fig. 2-9. A rhombic primitive cell can be constructed using the right prism whose base contains the  $60^\circ$  and  $120^\circ$  angles seen in the figure.

The trigonal *R* system is also rhombohedral and in this sense it is similar to the hexagonal system. Crystals of this system have at least one 3-fold axis, since the angles between the primitive translation vectors are equal (but not  $90^\circ$ ). Cubic crystals are more highly symmetric in that crystals of this system have at least four 3-fold axes along cube diagonals. There are three cubic Bravais lattices; we will have more to say about the symmetry elements of the cubic system a little later. One can imagine a few other configurations than those we have discussed, but in each case these reduce to one of those shown in Fig. 2-9. There are only 14 unique Bravais or space lattices. The various identifying features, angles, and lengths of these 14 are listed in Fig. 2-9 under the figures. Notice from our discussion that the 14 Bravais lattices fall into seven systems depending upon the type and number of rotation axes present.

Rotation symmetry is therefore most important in classifying crystals according to these seven different systems: triclinic, monoclinic, orthorhombic, trigonal, tetragonal, hexagonal, or cubic.

## 2-6 MILLER INDICES

A widely used convention for designating lattice planes and directions in a crystal is that of *Miller indices*. Let us use the cubic system by way of illustration, since a cube is a highly symmetric structure which has several prominent axes of symmetry. We choose our reference or crystallographic axes perpendicular to the cube faces. The Miller indices for the various planes are referred to these axes and are found with the help of Fig. 2-10 as follows: (1) Choose the reference, or  $z$  axis, perpendi-



**FIGURE 2-10.** Illustrating the principal planes and their notation for a cubic crystal. In each case the first number in the parentheses is the reciprocal of the intercept along the  $x$  axis, the second the reciprocal of the intercept along the  $y$  axis, and the third the same for the  $z$  axis.

cular to a cube face as shown. (2) Measure the positions of atoms along the axis in terms of a lattice constant. This is equivalent to choosing a parametral plane  $abc$  the  $(111)$  plane. (3) Find the intercepts of any plane along the axes in terms of  $abc$ . Take reciprocals of these numbers and reduce to the smallest three integers. These are the Miller indices

of the plane in question. The Miller indices of the various important planes for a cube are shown in Fig. 2-10. Here we have referred these planes to a particular set of axes, but for any crystal structure, a set of axes can be found for which the Miller indices reduce to simple integers or zero. This is known as the law of rational indices.

For the purpose of specifying the Miller indices of a hexagonal crystal, one chooses four axial directions  $a_1$ ,  $a_2$ ,  $a_3$ ,  $c$ . In this case a plane is specified by four numbers as indicated in Fig. 2-11.



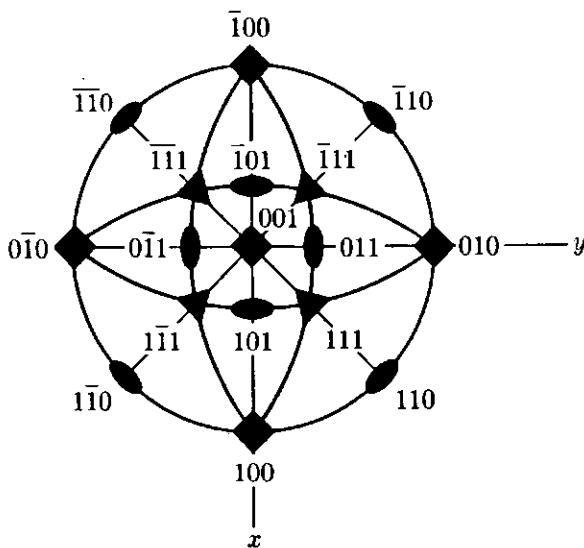
**FIGURE 2-11.** Illustrating the choice of axial directions and Miller indices for a hexagonal crystal.

A given direction in a crystal is specified by the smallest set of integers having the same ratio as the components or direction cosines of a vector drawn in that direction. In a cubic crystal, the indices of a plane are the same numbers used to specify the normal to the plane. Directions are conveniently indicated by square rather than round brackets. For example, the [111] direction for a cube is perpendicular to the (111) plane. The  $c$  axis in the case of a hexagonal lattice is the [0001] direction. If we speak in general about equivalent directions or equivalent planes, we use (in the cubic case, for example) the notation  $\langle 110 \rangle$  or  $\{110\}$  respectively. We turn next to stereographic projections which allow one to represent

the various principal directions, or any direction in the crystal, by points on a plane figure.

## 2-7 STEREOGRAPHIC PROJECTIONS

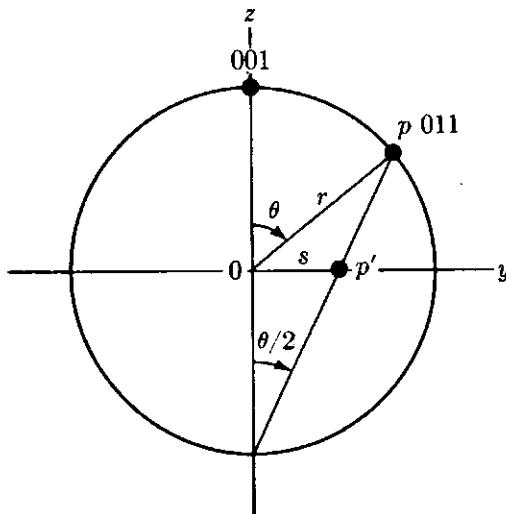
A stereographic projection is a kind of bird's-eye view of points on a sphere obtained by looking at the sphere from above the north pole ( $z$  axis). The point in question (say, a lattice point to which a point group operation applies) is placed at the center of the sphere. The symmetry axes, which may be normal to crystallographic planes, pass through the center point and intersect the sphere at points called *poles*. The position of these poles is then projected stereographically onto a plane as shown in Fig. 2-12,<sup>3</sup> which is a vertical section through the sphere of radius  $r$ . The projection of point  $P$  is point  $P'$ .



**FIGURE 2-12.** Stereogram of the  $m\bar{3}m$  or most symmetric cubic point group. 2-fold axes of rotation are indicated by  $\circ$ , 3-fold by  $\triangle$ , and 4-fold by  $\square$ .

An indexed stereogram of the various rotation axes for the most symmetric cubic structure is shown in Fig. 2-13.<sup>2</sup> This is, in fact, a stereogram for the  $m\bar{3}m$  point group that will be discussed below. Directions are conventionally designated by indices as discussed in the previous section. Notice that the  $z$  axis points up out of the paper in the  $[001]$  direction. The unique characteristic of all five cubic groups is the occurrence of triad axes in the  $\langle 111 \rangle$  directions. The directions of the various tetrad and diad axes can be seen without difficulty. The diad axis at the point

[011] in the stereogram is about 0.4 rather than halfway from the center to the 010 point. This distance,  $s$ , is obtained by setting  $\theta = 45^\circ$  in the formula  $s = r \tan (\theta/2)$  as seen in Fig. 2-12. Notice that the points representing certain poles in Fig. 2-13 lie along common lines or circles. These are great circles on the sphere and each represents what is called a *zone*. The planes of a given zone all have a common parallel direction, the zone axis.



**FIGURE 2-13.** A vertical section through the unit sphere showing how point  $P$  projects to point  $P'$ .

## 2-8 THE THIRTY-TWO CRYSTALLOGRAPHIC POINT GROUPS

As was suggested earlier a point group is a collection of operations, such as rotations, reflections, and inversions, which leaves at least one point of the crystal (crystal lattice or molecule) fixed and all other points invariant. There are only 32 crystallographic point groups in all. These are listed according to the older Schoenflies notation and the more modern Hermann–Mauguin notation in Table 2-2.

Notice that the groups in Table 2-2 are arranged according to crystal system, and for this purpose the kind and number of rotation or rotation-inversion axes are most important. The Schoenflies notation suggests the operations involved or the individual elements of the group. For example,  $C_n$  stands for a single  $n$ -fold rotation axis. The number of elements or order of the group is given by  $n$ . If  $n = 6$ , the symmetry operations involve rotations through  $60^\circ$ . The group contains the elements or operations  $C_6$ ,  $(C_6)^2 = C_3$ ,  $(C_6)^3 = C_2$ ,  $(C_6)^4 = (C_3)^{-1}$ ,  $(C_6)^5 = (C_6)^{-1}$ , and  $(C_6)_6 = E$ , where this last symbol stands for the identity element. Stereo-

TABLE 2-2. Equivalent Notation for the 32 Crystallographic Point Groups

| System          | Schoenflies <sup>a</sup>  | Short form <sup>b,c</sup> | Long form <sup>c</sup>                | Explanation of long form notation <sup>b</sup> position in point-group symbol   |   |  |
|-----------------|---------------------------|---------------------------|---------------------------------------|---|---|--|
|                 |                           |                           |                                       | Primary   | Secondary                                   | Tertiary   |
| Triclinic       | $C_1$<br>$S_2(C_i)$       | $\frac{1}{\bar{1}}$       | $\frac{1}{\bar{1}}$                   | Only one symbol which denotes all directions in the crystal                     |   |  |
| Monoclinic      | $C_2$<br>$C_{1h}$         | 2<br>$m$                  | 2<br>$m$                              | The symbol gives the nature of the unique diad axis (rotation and/or inversion) |   |  |
|                 | $C_{2h}$                  | $2/m$                     | $\frac{2}{m}$                         |   |   |  |
| 32 Orthorhombic | $C_{2v}$<br>$D_2(V)$      | $2mm$<br>222              | $2mm$<br>$222$                        | Diad ( $r, /i$ ) along<br>$x$ axis  | Diad ( $r, /i$ ) along<br>$y$ axis          | Diad ( $r, /i$ ) along<br>$z$ axis                 |
|                 | $D_{2h}(V_h)$             | $mmm$                     | $\frac{2}{m} \frac{2}{m} \frac{2}{m}$ |   |   |  |
| Tetragonal      | $C_4$<br>$S_4$            | $\frac{4}{\bar{4}}$       | $\frac{4}{\bar{4}}$                   | Tetrad ( $r, /i$ ) along<br>$z$ axis  | Diads ( $r, /i$ ) along<br>$x$ and $y$ axes | Diads ( $r, /i$ ) along<br>[110] and [110]<br>axes |
|                 | $C_{4h}$                  | $4/m$                     | $\frac{4}{m}$                         |   |   |  |
|                 | $C_{4v}$<br>$D_{2d}(V_d)$ | $4mm$<br>$\bar{4}2m$      | $4mm$<br>$\bar{4}2m$                  |   |   |  |
|                 | $D_4$                     | $422$                     | $422$                                 |   |   |  |
|                 | $D_{4h}$                  | $4/mmm$                   | $\frac{4}{m} \frac{2}{m} \frac{2}{m}$ |   |   |  |

TABLE 2-2. Equivalent Notation for the 32 Crystallographic Point Groups (Continued)

| System    | Schoenflies <sup>a</sup> | Short form <sup>b,c</sup> | Long form <sup>c</sup>          | Explanation of long form notation <sup>b</sup> position in point-group symbol |   |
|-----------|--------------------------|---------------------------|---------------------------------|---|---|
|           |                          |                           |                                 | Primary   | Secondary   |
| Trigonal  | $C_3$                    | $\frac{3}{\bar{3}}$       | $\frac{3}{\bar{3}}$             | Triad ( $r/i$ ) along $z$ axis  | Diads ( $r/i$ ) along $x, y$ , and $u$ axes       |
|           | $S_6(C_{3h})$            | $3m$                      | $3m$                            |   |   |
|           | $C_{3v}$                 |                           |                                 |   |   |
|           | $D_{3d}$                 | $\bar{3}m$                | $\bar{3}\frac{2}{m}$            |   |   |
|           | $D_8$                    | 32                        | 32                              |   |   |
| Hexagonal | $C_6$                    | 6                         | 6                               | Hexad ( $r/i$ ) along $z$ axis  | Diads ( $r/i$ ) along $x, y$ and $u$ axes         |
|           | $C_{3h}$                 | $\bar{6}$                 | $\bar{6}$                       |   |   |
|           | $C_{6h}$                 | $6/m$                     | $6/\underline{m}$               |   |   |
|           | $C_{6v}$                 |                           |                                 |   |   |
|           | $D_{3h}$                 | $6mm$                     | $6m\underline{m}$               |   |   |
|           | $D_6$                    | $\bar{6}m2$               | $\bar{6}m2$                     |   |   |
|           | $D_{6h}$                 | 622                       | 622                             |   |   |
|           |                          |                           |                                 |   |   |
|           |                          |                           |                                 |   |   |
|           |                          |                           |                                 |   |   |
| Cubic     | $T$                      | 23                        | 23                              | Diads or tetrads ( $r/i$ ) along $\langle 111 \rangle$ axes                   | Triads ( $r/i$ ) along $\langle 111 \rangle$ axes |
|           | $T_h$                    | $m3$                      | $\frac{2}{m}\bar{3}$            |   |   |
|           | $T_d$                    | $\bar{4}3m$               | $\bar{4}3m$                     |   |   |
|           | $O$                      | 432                       | 432                             |   |   |
|           | $O_h$                    | $m3m$                     | $\frac{4}{m}\bar{3}\frac{2}{m}$ |   |   |

<sup>a</sup> A. Schoenflies, *Krystallsysteme und Krystallstruktur* (Leipzig, 1891).

<sup>b</sup> International Tables for X-ray Crystallography (Kynock Press, Birmingham, 1952, Vol. I.)

<sup>c</sup> C. Hermann, Z. Krist. **68**, 257 (1928); **76**, 559 (1931); C. Mauguin, Z. Krist. **76**, 542 (1931).

grams for the 32 point groups are shown in Fig. 2-14, and the various  $C_n$  rotation as well as rotation-inversion axes  $C_{ni}$  are indicated by appropriate symbols.

The groups  $C_{nv}$  contain a number of symmetry related vertical mirror planes  $\sigma_v$  in addition to the  $C_n$  rotation axis. These mirror planes are indicated by solid radial lines on the stereograms. The groups  $C_{nh}$  contain a horizontal mirror plane  $\sigma_h$  indicated by a solid rather than dotted stereogram circle. Groups labeled by  $D_n$ ,  $D_{nd}$ , and  $D_{nh}$  contain  $n$  2-fold axes perpendicular to a  $C_n$  axis. The subscript  $d$  stands for diagonal reflection planes that bisect the angles between the 2-fold axes, and  $h$  again stands for horizontal mirror planes  $\sigma_h$ . Groups of the highly symmetric cubic system are labeled either by  $T$ , which stands for tetrahedral, or  $O$ , for octahedral. The group  $T$  contains the 12 rotational operations which bring a regular tetrahedron into itself—similarly for the octahedron in which 24 operations are involved.

The Hermann–Mauguin symbols were proposed so that one could see at a glance the important symmetry elements of the group. Whereas the short Hermann–Mauguin symbol contains just enough symbols to unambiguously denote the group, the full or long form symbol is more descriptive. An explanation of the long form notation is given in Table 2-2. For example, consider the most symmetric cubic group which is designated either by

$$m3m \quad \text{or} \quad \frac{4}{m} \bar{3} \frac{2}{m}.$$

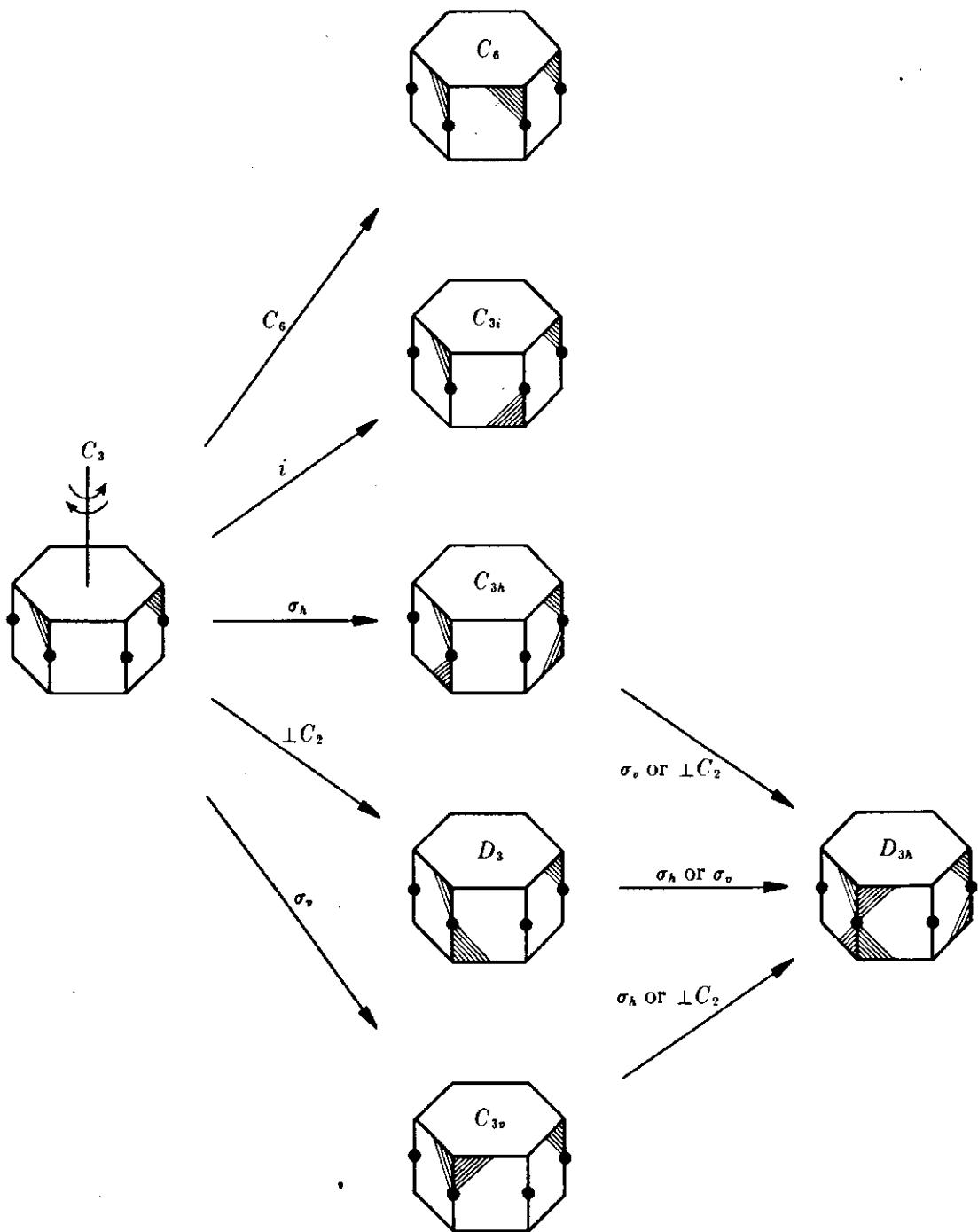
The latter notation indicates that the group is characterized by a tetrad axis together with perpendicular mirror planes, a triad axis including a center of symmetry, and diad axes each perpendicular to mirror planes. These symmetry elements can be seen in the stereogram of Fig. 2-14. The symbols designate the group but do not completely describe it. For instance, there are four tetrad axes related by symmetry, the center of inversion applies to the six diad axes as well as to the triad axes, etc. Further discussion is to be found in any one of several references [8–10].

Group theory arguments can be used to show that there are only 32 crystallographic point groups [11]. It is perhaps useful to point out that all 32 groups can be discovered by starting with the trivial group  $C_1$  and systematically adding in succession the various symmetry elements allowed by lattice periodicity. At each stage, the resulting group of combined operations is examined to see if it is in agreement with translational symmetry and if the group is the same as or different from those obtained starting from other symmetries. The process converges in the sense that only a finite number of crystallographic point groups, i.e., 32, are generated.

| Triclinic | Monoclinic and orthorhombic | Trigonal | Tetragonal | Hexagonal | Cubic                |
|-----------|-----------------------------|----------|------------|-----------|----------------------|
|           |                             |          |            |           |                      |
|           |                             |          |            |           |                      |
|           |                             |          |            |           |                      |
|           |                             |          |            |           | $\Delta = \triangle$ |
|           |                             |          |            |           |                      |
|           |                             |          |            |           |                      |
|           |                             |          |            |           |                      |

**FIGURE 2-14.** Stereograms for each of the 32 crystallographic point groups. Equivalent points above and below the plane are indicated by + and ○, respectively.

The process is illustrated in Fig. 2-15 which shows five ways that symmetry elements can be added to the point group  $C_3$  [12]. The symmetry involved in each case may be seen by studying the drawing and noting the equivalent positions of the shaded area of a face. Now, each of the five groups on the right can be obtained by adding to the group on the left an  $n$ -fold axis  $C_n$ , an inversion center  $i$ , a horizontal mirror plane  $\sigma_h$ , a



**FIGURE 2-15.** A diagram indicating how various point groups can be found by adding symmetry elements to the group  $C_3$  as discussed in the text. (After E. P. Wigner [12].)

perpendicular 2-fold axis, or a vertical mirror plane  $\sigma_v$ . In the first case, that of adding a 6-fold rotation axis, the order of the 3-fold rotation axis is increased to 6-fold with the result that a new group  $C_6$  arises. The addition of an inversion center to  $C_3$  is the same as rotation about the vertical axis through  $2\pi/6$  radians plus reflection in a horizontal plane. This clearly results in the group  $C_{3i}$ . Reflection in a horizontal plane gives  $C_{3h}$ . A 2-fold axis added perpendicular to the 3-fold yields the group  $D_3$ . In this last case two other horizontal 2-fold axes are symmetry related to the first diad axis. Finally, reflection in a vertical plane through the 3-fold axis, and in two other symmetry related vertical planes, gives the group  $C_{3v}$ . Notice that the vertical, 3-fold symmetry axis is to be found in each of five resulting groups. That is to say, the group  $C_3$  is a subgroup of each of the others. Also, it should be remarked that the number of equivalent points (order of the group) increases in going from  $C_3$  which has order 3 to any one of the five groups which have order 6. One of several groups in the last column is shown. These have order 12.

It can be seen that the group  $D_{3h}$  results by adding a vertical mirror plane to  $C_{3h}$ , a horizontal or vertical mirror plane to  $D_3$ , or by adding either a horizontal mirror plane or perpendicular diad axis to  $C_{3v}$ . This last higher-order group,  $D_{3h}$ , is much more symmetric than the starting group. Additions can likewise be made to  $C_6$ , and  $C_{3i}$ . It is a useful exercise to derive five remaining groups leading up to and including  $D_{6h}$ .

## 2-9 POINT-GROUP SYMMETRY AND PHYSICAL PROPERTIES

The 32 point-group symmetries and corresponding crystal classes which we have just studied are revealed by the physical properties of solids. Herein lies the importance of point-group symmetry [13]. Let us first consider properties such as pyroelectric coefficient, conductivity or resistivity, susceptibility, elastic constants, etc., as listed in Table 2-3. Initially we limit ourselves to *linear* relations between some physical quantity such as current density  $j$  (electrical, thermal, or diffusion) and a forcing term or gradient such as electric field  $E$ . In general the crystalline property is a tensor of rank shown in the table. However, symmetry introduces certain simplifications, so that in this sense a proper description of the tensor property contains at least the point-group symmetry characteristic of the crystal. This will be discussed in detail for electrical conductivity in the next section, for stress and strain in Chapter 5 and for susceptibility or dielectric response in Chapter 7.

Let us consider a few examples that will illustrate the power of symmetry arguments. The first of these has to do with the phenomenon of

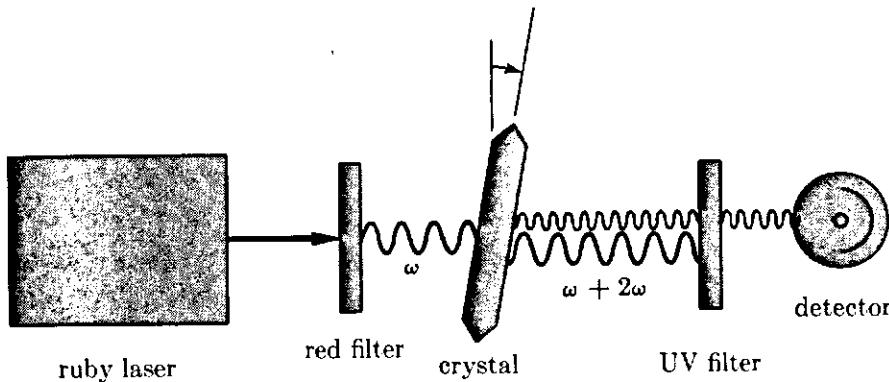
pyroelectricity. The opposite faces of a few crystalline substances become electrically charged simply as a result of a change in temperature. One such substance is the mineral tourmaline, the opposite faces of which are sometimes observed to attract and hold dust particles because of electrical charge. Pyroelectricity is described by pyroelectric coefficients which relate electric polarization (a vector) to temperature change (a scalar) as indicated in the first row of Table 2-3. We can predict right off that such a phenomenon can occur only in crystals which lack an inversion center or center of symmetry. This follows because, when an inversion center is present, points on opposite faces of the crystal must be equivalent. One face cannot become positively charged and the other face negatively charged simply as a result of a change in temperature (uniform throughout the crystal).

TABLE 2-3. *Linear Physical Properties of Solids. After C. S. Smith [13]*

| Property and symbol <sup>a</sup>            | Rank of tensor | Number of independent components | Dependent physical quantity            | Independent variable            |
|---|----------------|----------------------------------|--|---------------------------------|
| pyroelectric coefficient $\underline{p}$    | 1              | 3                                | electric polarization $d\underline{P}$ | temperature change $d\theta$    |
| conductivity $\underline{\sigma}$           | 2              | 6                                | current density $\underline{j}$        | field $\mathbf{E}$              |
| resistivity $\underline{\rho}$              | 2              | 6                                | field $\mathbf{E}$                     | current density $\underline{j}$ |
| susceptibility $\underline{x}$              | 2              | 6                                | electric polarization $\underline{P}$  | electric field $\mathbf{E}$     |
| thermal expansion $\underline{\alpha}$      | 2              | 6                                | strain $\underline{e}$                 | temperature change $d\theta$    |
| piezoelectric coefficient $\underline{d}$   | 3              | 18                               | electric polarization $\underline{P}$  | stress $\underline{T}$          |
| elastic stiffness constants $\underline{c}$ | 4              | 21                               | stress $\underline{T}$                 | strain $\underline{e}$          |
| elastic compliance $\underline{s}$          | 4              | 21                               | strain $\underline{e}$                 | stress $\underline{T}$          |
| piezoresistance $\underline{\pi}$           | 4              | 21                               | resistivity change $\Delta\rho$        | stress $\underline{T}$          |

<sup>a</sup> Bar under a quantity indicates the quantity is a tensor.

Certain substances are piezoelectric so that when opposite faces are compressed a voltage is developed across these faces. Piezoelectricity is described by a tensor that relates the electric polarization vector to the six components of a stress tensor as indicated in the sixth row of Table 2-3. Again symmetry arguments tell us that piezoelectricity cannot occur in any crystal which contains an inversion center. Points on opposite faces of the compressed crystal must still be equivalent. Cubic insulating crystals such as the alkali halides have an inversion center so that they are not piezoelectric. Quartz, CdS, and ZnS are among substances which do show piezoelectricity. Finally, it should be stressed that the lack of an inversion center does not by itself guarantee measurable piezoelectric behavior.



**FIGURE 2-16.** Apparatus for detecting second harmonic light generation. In the case of a ruby laser  $\omega$  corresponds to a wavelength of 6940 Å.

As a further example of this type of symmetry argument, let us consider the nonlinear optical phenomenon of second harmonic generation [14, 15]. This phenomenon became both readily observable and important in technology with the advent of coherent light sources such as the ruby laser. This device emits red light at a wavelength of 6940 Å with intensity in the range of kilowatts to megawatts per cm<sup>2</sup>. Figure 2-16 shows the relatively simple apparatus used to observe second harmonic generation. The red filter excludes stray violet or ultraviolet light, such as might be produced by the laser pump source. The uv filter excludes the incident red light at frequency  $\omega$  corresponding to 6940 Å but passes light generated in the crystal at  $2\omega$  corresponding to about 3500 Å. Efficient filtering and the wide separation between  $\omega$  and  $2\omega$  assure that a very small second harmonic component can be detected. In practice one arranges the crystal so that it can be rotated in angle as shown which causes the harmonic output to vary periodically in angle due to dispersion and phase coherence between components within the crystal.

The generation of second and higher harmonics depends upon the non-

linear relation between polarization  $\mathbf{P}$  and electric field  $\mathbf{E}$ . For purposes of argument [14], consider a scalar relation between  $\mathbf{P}$  and  $\mathbf{E}$  as follows:

$$P = \chi E(1 + a_1 E + a_2 E^2 + \dots), \quad (2-8)$$

where  $\chi$  is the linear susceptibility as used in Table 2-3 and  $a_1$ ,  $a_2$ , etc., are very small nonlinear coefficients. The second term in the expansion Eq. (2-8) is quadratic in  $E$ . For a sinusoidal time dependence,  $E = E_0 \sin \omega t$ , this second term gives rise to the following contribution to the polarization

$$P_2 = \chi a_1 E_0^2 \sin^2 \omega t = \frac{\chi a_1 E_0^2}{2} (1 - \cos 2\omega t). \quad (2-9)$$

The 1 in the bracket is analogous to the direct current from a square law detector; the second term gives rise to the second harmonic content. One can now argue by symmetry that significant second (or higher even) harmonics will not be generated, if the crystal is isotropic or has an inversion center. When an inversion center is present,  $P$  must reverse sign for reversal of  $E$ ; the coefficients  $a_1$  must therefore vanish. One expects harmonic generation in quartz but not in calcite or alkali halide crystals (although harmonic generation may not be entirely absent in these materials at very high power levels). The phenomena we are discussing here are of electronic origin and can be described by adding third- and higher-order potential terms to the Lorentz equations for polarizability, which will be discussed in Section 8-2. Let us return to linear properties and discuss the electrical conductivity tensor.

## 2-10 ELECTRICAL CONDUCTIVITY AND CRYSTAL SYMMETRY

In elementary physics one learns that current density  $\mathbf{j}$  is related to electric field  $\mathbf{E}$  by means of a scalar  $\sigma$  as follows

$$\mathbf{j} = \sigma \mathbf{E}. \quad (2-10)$$

In general, however,  $\sigma$  is not a scalar but a second rank tensor as listed in Table 2-3. The relation between the components of  $\mathbf{E}$  and the components of  $\mathbf{j}$  is the following:

$$\begin{aligned} j_x &= \sigma_{xx} E_x + \sigma_{xy} E_y + \sigma_{xz} E_z, \\ j_y &= \sigma_{yx} E_x + \sigma_{yy} E_y + \sigma_{yz} E_z, \\ j_z &= \sigma_{zx} E_x + \sigma_{zy} E_y + \sigma_{zz} E_z. \end{aligned} \quad (2-11)$$

According to a theorem due to Onsager [16], tensors such as  $\sigma$ , which represent physical quantities, are symmetric, that is

$$\sigma_{ij} = \sigma_{ji}. \quad (2-12)$$

As pointed out by Smith [13], this symmetrical property of tensors can also be regarded as an experimental fact. Because of Eq. (2-12), the nine components of the conductivity tensor reduce to six—even in the case of triclinic crystals that do not possess an axis of symmetry.

The conductivity tensor of Eq. (2-11) is referred to some set of coordinates in the crystal. In general, it is possible to transform to another set of coordinates which leave  $\sigma$  diagonal. In this case, not only the three diagonal components of the transformed  $\sigma$  need be specified, but also the three direction cosines which specify the orientation of the principal axes. In general, six numbers and therefore six separate measurements must be made.

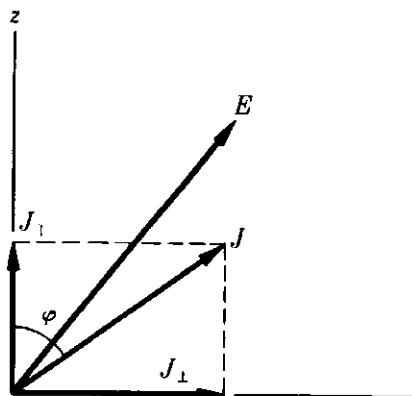
On the other hand, nearly all metallic crystals possess at least one axis of symmetry, and this simplifies the tensor and reduces the number of independent coefficients. We give the arguments for this reduction in the case of tetragonal crystals that have a 4-fold axis of symmetry, assumed to lie in the direction of our chosen reference axis.

Consider first what we mean experimentally by electrical conductivity. Usually, a measurement is made by preparing a long thin sample, for example, a wire. The current  $j$  is constrained to the long direction of the specimen that is at some previously determined angle  $\varphi$ , with respect to the reference or crystallographic axis. If the material is anisotropic, the direction of electric field  $E$  is not necessarily the same as  $j$ . Determination of the longitudinal component of  $E$  is made by measuring the potential drop down the length of the sample under conditions of current flow. By conductivity with current flow in the direction  $\varphi$ , we mean the ratio of  $j$  to the component of  $E$  in the direction of  $j$ , i.e.,

$$\sigma(\varphi) = \frac{j}{E(\varphi)}. \quad (2-13)$$

If it happens that the sample is prepared so that  $j$  lies in a plane to which the axis of symmetry is perpendicular, only one number  $\sigma_{\perp}$  need be specified. This can be seen as follows: In the perpendicular plane, for tetragonal symmetry there are two equivalent directions which will be called the  $x$  and the  $y$  axes. If these directions are equivalent, the  $x$  and  $y$  conductivities must be the same, i.e.,  $\sigma_x = \sigma_y = \sigma_{\perp}$ . Moreover, if current is constrained to the  $x$  axis,  $j = j_x \hat{i}$ , then  $E$  also lies along the  $x$  axis, i.e.,  $E = E_x \hat{i}$ . This can be shown by arguing that the current vector  $j = j_x \hat{i}$  will not give rise to a  $y$  component of  $E$  because the  $+y$  and  $-y$

directions are equivalent. In other words, we cannot specify the direction of  $E_y$  as  $+y$  and also have 4-fold rotation symmetry about the  $z$  axis;  $E_y$  must be zero. Similar arguments apply for  $j$  along the  $y$  axis. If now  $j$  lies in the  $x - y$  plane making an arbitrary angle  $\theta$  with respect to the  $x$  axis, the same conductivity applies as follows: Decompose  $j$  into components  $j_x = j \cos \theta$  and  $j_y = j \sin \theta$ . We just saw that a conductivity  $\sigma_{\perp}$  applied along these directions, so the field strength components can be written as  $E_x = j_x/\sigma_{\perp}$  and  $E_y = j_y/\sigma_{\perp}$ . If we now substitute for  $j_x$  and  $j_y$  and project back onto the direction of  $j$ , the result is  $E = (j \cos^2 \theta + j \sin^2 \theta)/\sigma_{\perp}$ . Therefore, the conductivity in the  $j$  direction is  $\sigma = j/E = \sigma_{\perp}$ . To summarize, we need specify only one conductivity component  $\sigma_{\perp}$  if  $j$  lies in a plane to which the axis of symmetry is perpendicular.



**FIGURE 2-17.** Showing current density  $j$  making an angle  $\varphi$  with respect to the symmetry axis ( $z$  axis).

Now consider the situation that  $j$  does not lie in the  $x - y$  plane but makes some arbitrary angle  $\varphi$  with respect to the symmetry axis ( $z$  axis) as shown in Fig. 2-17. Here the electric vector  $E$  is not in the same direction as  $j$ . The components of  $j$  along and perpendicular to the axis are  $j_{\parallel} = j \cos \varphi$  and  $j_{\perp} = j \sin \varphi$ , respectively. These currents can also be written in terms of conductivity coefficients  $j_{\parallel} = \sigma_{\parallel}E_{\parallel}$  and  $j_{\perp} = \sigma_{\perp}E_{\perp}$ . Solving for  $E_{\parallel}$  and  $E_{\perp}$ , it follows that

$$E_{\parallel} = \frac{j \cos \varphi}{\sigma_{\parallel}} \quad (2-14)$$

and

$$E_{\perp} = \frac{j \sin \varphi}{\sigma_{\perp}}. \quad (2-15)$$

These components can now be projected back onto the  $j$  or  $\varphi$  direction to give an expression for  $E(\varphi)$ :

$$E(\varphi) = \frac{j \cos^2 \varphi}{\sigma_{\parallel}} + \frac{j \sin^2 \varphi}{\sigma_{\perp}}. \quad (2-16)$$

This last expression could be solved for  $j$  and the conductivity computed from Eq. (2-13). Here, however, it is a little simpler to define the resistivity as the reciprocal of conductivity  $\rho(\varphi) \equiv 1/\sigma(\varphi)$  so that Eq. (2-16) yields the following result:

$$\rho(\varphi) = \frac{E(\varphi)}{j} = \rho_{\parallel} \cos^2 \varphi + \rho_{\perp} \sin^2 \varphi, \quad (2-17)$$

where the longitudinal and perpendicular coefficients are  $\rho_{\parallel} = 1/\sigma_{\parallel}$  and  $\rho_{\perp} = 1/\sigma_{\perp}$ , respectively.

In the case of trigonal and also hexagonal crystals, similar arguments can be given. Again these show that only two coefficients need be specified. On the other hand, the less symmetric orthorhombic and monoclinic systems require three and five conductivity coefficients, respectively. In the case of highly symmetric structures such as cubic crystals, the directions along and perpendicular to the cube axis are equivalent. Therefore, one can immediately say that  $\sigma_{\parallel} = \sigma_{\perp} = \sigma$  and only one coefficient need be specified. It follows from Eq. (2-17) that the electrical conductivity (or resistivity) of cubic crystals is isotropic.

Table 2-4 shows the observed anisotropy of different metals at room temperature. These results are for single crystals. In the case of polycrystalline samples, the anisotropy of grains would average out over different orientations so that the material would appear highly isotropic.

**TABLE 2-4. Room Temperature Resistivity Coefficients for Metallic Crystals Belonging to Different Systems. Data from International Critical Tables, 6, 135 (1929)**

| Metal      | System     | $\rho_{\parallel}$<br>( $10^{-6} \Omega\text{-cm}$ ) | $\rho_{\perp}$<br>( $10^{-6} \Omega\text{-cm}$ ) |
|------------|------------|--|--|
| Sn (white) | tetragonal | 14.3   | 9.90   |
| Bi         | trigonal   | 138  | 109  |
| Zn         | hexagonal  | 5.83   | 5.39   |
| Cd         | hexagonal  | 8.30   | 6.80   |
| Hg         | hexagonal  | 17.8   | 23.5   |
| Cu         | cubic      |  | 1.15   |
| W          | cubic      |  | 5.48   |

Let us now turn from the subject of point symmetry and physical properties to a discussion of the symmetry elements which apply to actual crystal structures.

## 2-11 SPACE GROUPS AND NOTATION

It can be readily seen that as one places a basis of atoms or molecules on the points of the various Bravais lattices, the number of symmetry operations and combinations of symmetry operations greatly increases. In fact, crystal structures involve new types of symmetry elements, and these together with the point groups lead to 230 *space groups*. Before describing these new symmetry elements, let us make a few remarks about the nature of a basis.

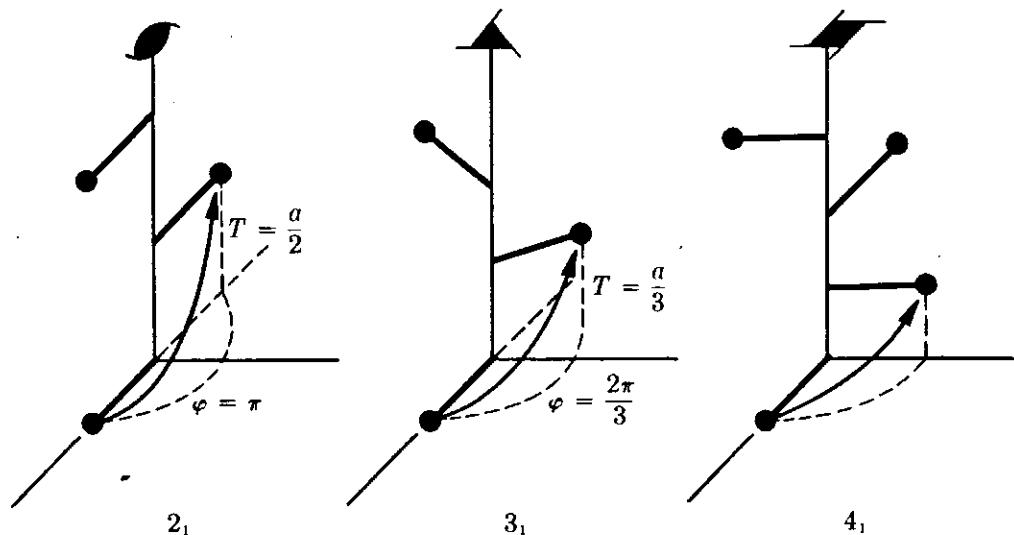
In principle, we could place any kind of basis, a five-pointed figure like a starfish for example, at the points of a Bravais lattice to form a structure. This does not happen physically, however. The symmetry of the basis *as it exists in the crystal* is closely related to the symmetry of the Bravais lattice. No symmetry elements can be involved that are not part of the symmetry of the Bravais lattice. It is also true that the lattice in equilibrium is held together by forces between atoms. This means that the basis should contain at least one of the symmetry elements that distinguishes the particular Bravais lattice from those of lower symmetry. Otherwise, the structure would not have a minimum energy configuration characteristic of the system involved. An infinitesimal distortion could alter the system to one of lower symmetry. This is to say that a hierarchy exists among the seven crystal systems [17]. With these preliminary remarks about the nature of a basis let us describe the new elements needed to define space groups.

The first of the new symmetry elements needed for space groups is the *screw axis*. Such an axis is a kind of rotation axis which must be chosen parallel to a translation direction in the crystal. The operation is, in fact, a combination of rotation,  $\varphi$ , and translation,  $T$ , as seen in Fig. 2-18. The unique screw axes are  $2_1, 3_1, 3_2, 4_1, 4_2, 4_3, 6_1, 6_2, 6_3, 6_4, 6_5$ , where the main number  $n$ , indicates the manifoldness of the rotation axis and the subscript indicates the value of an integer in the equation

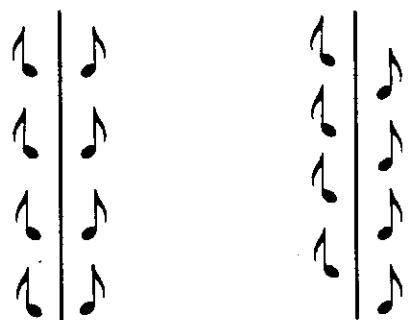
$$nT = ja. \quad (2-18)$$

This equation states that after  $n$  rotations, each through an angle  $\varphi$ , the lattice is translated a multiple of the lattice parameter,  $ja$ . The amount of translation for any one rotation is  $T = (j/n)a$ . In Fig. 2-18, for

example,  $T = a/2$  for  $2_1$ ,  $a/3$  for  $3_1$ , and  $a/4$  for  $4_1$ . Certain of the screw axes are related to each other as being merely right and left handed. For example, the  $3_1$  and  $3_2$  are merely right- and left-handed operations of the same kind. The axes  $4_1$  and  $4_3$  as well as  $6_1$  and  $6_5$  are likewise related.



**FIGURE 2-18.** Showing how atoms are brought into coincidence by rotation and translation along a screw axis. Three different screw axes are shown.  $a$  is the lattice spacing and  $\varphi$  an angle of rotation.



Reflection plane      Axial glide plane

**FIGURE 2-19.** Illustrating the difference between a reflection plane and an axial glide plane.

A *glide plane* consists of a reflection plus a translation in a direction parallel to the reflection. Axial glide can be described in a simple two-dimensional picture as shown in Fig. 2-19. The possible glide planes found in crystal structures are listed in Table 2-5.

**TABLE 2-5.** Listing the Various Types of Glide Planes, Their Symbols and Translation Components

| Type           | Symbol | Translation component $T$   |
|----------------|--------|---|
| Axial          | $a$    | $\frac{a}{2}$   |
| Axial          | $b$    | $\frac{b}{2}$   |
| Axial          | $c$    | $\frac{c}{2}$   |
| Diagonal glide | $n$    | $\frac{a}{2} + \frac{b}{2}, \frac{b}{2} + \frac{c}{2}$ , or $\frac{c}{2} + \frac{a}{2}$ |
| Diamond glide  | $d$    | $\frac{a}{4} + \frac{b}{4}, \frac{b}{4} + \frac{c}{4}$ , or $\frac{c}{4} + \frac{a}{4}$ |

We are now in a position to discuss the allowed space groups. Altogether a total of 230 space groups are arrived at by considering the various combinations involving the 32 point groups, the screw axes, and glide planes, as well as the different Bravais or space lattices. These 230 space groups are described along with stereograms and equivalent points in

**TABLE 2-6.** Space Groups of Some Common Crystals

| Substance      | Hermaan-Mauguin                        | Schoenflies |
|----------------|--|-------------|
| NaCl, AgBr     | $F\frac{4}{m}\bar{3}\frac{2}{m}$       | $O_h^5$     |
| CsCl (cubic)   | $P\frac{4}{m}\bar{3}\frac{2}{m}$       | $O_h^1$     |
| C diamond      | $F\frac{4_1}{d}\bar{3}\frac{2}{m}$     | $O_h^7$     |
| C graphite     | $P\frac{6_3}{m}\frac{2}{m}\frac{2}{c}$ | $D_{6h}^4$  |
| ZnS (blende)   | $F\bar{4}3m$                           | $T_d^2$     |
| ZnS (wurtzite) | $P6_3mc$                               | $C_{6v}^4$  |
| ZnO            | $P6_3mc$                               | $C_{6v}^4$  |
| CdS (hex)      | $P6_3mc$                               | $C_{6v}^4$  |
| CdS (cubic)    | $F\bar{4}3m$                           | $T_d^2$     |
| NiAs           | $P\frac{6_3}{m}\frac{2}{m}\frac{2}{c}$ | $D_{6h}^4$  |
| BN             | $P\frac{6_3}{m}\frac{2}{m}\frac{2}{c}$ | $D_{6h}^4$  |
| Cu             | $F\frac{4}{m}\bar{3}\frac{2}{m}$       | $O_h^5$     |

standard references on the subject [8]. Space groups are most important in the study of the microscopic properties of crystals. The point symmetries at various special positions within the lattice, as well as the existence of screw axes and glide planes, can be determined from a knowledge of the space-group symbol for a substance.

Each of the 230 space groups has an identifying symbol that again is designed to reveal at a glance the main features of the group. The space-group symbols begin with a capital letter, *P*, *C*, *F*, or *I*, which designates

**TABLE 2-7. The Distribution of Some Common Structure Types Among the 32 Crystal Classes**

| System       | Class       | Structure types   |
|--------------|-------------|---|
| Triclinic    | 1           |   |
|              | $\bar{1}$   | $\text{Al}_2\text{SiO}_5$   |
| Monoclinic   | 2           |   |
|              | $m$         | $\text{KNO}_2$  |
|              | $2/m$       |   |
| Orthorhombic | 222         |   |
|              | $mm2$       |   |
|              | $mmm$       | $\text{I}$ , $\text{Ga}$ , $\text{BaSO}_4$ , $\text{KNO}_3$   |
| Trigonal     | 3           | $\text{AsI}_3$  |
|              | $\bar{3}$   | Ilmenite ( $\text{FeTiO}_3$ )   |
|              | 32          | $\text{Se}$ , $\text{La}_2\text{O}_3$ , $\text{KAl}(\text{SO}_4)_2$   |
|              | $3m$        |   |
|              | $\bar{3}m$  | As, $\text{CdI}_2$ , $\text{Fe}_2\text{O}_3$ , Calcite ( $\text{CaCO}_3$ )  |
| Tetragonal   | 4           |   |
|              | $4/m$       | $\text{CaWO}_4$   |
|              | 422         |   |
|              | $4mm$       |   |
|              | $4/mmm$     | White tin, In, rutile( $\text{TiO}_2$ ), $\text{PbO}$ , $\text{ZrSiO}_4$  |
|              | $\bar{4}$   |   |
|              | $\bar{4}2m$ |   |
| Hexagonal    | 6           |   |
|              | $6/m$       | $\text{CeF}_3$  |
|              | 622         | $\text{ZnO}$ , $\text{NiAs}$ , $\text{Tl}_2\text{O}_3$ , $\text{SnI}_4$   |
|              | $6mm$       | $\text{Mg}$ , graphite, $\text{MoS}_2$  |
|              | $6/mmm$     |   |
|              | $\bar{6}$   |   |
|              | $\bar{6}m2$ |   |
| Cubic        | 23          | $\text{NaClO}_3$  |
|              | $m3$        | $\text{FeS}_2$  |
|              | 432         | $\beta\text{-Mn}$   |
|              | $\bar{4}3m$ | $\text{ZnS}$ , $\text{NaClO}_4$ , $\text{Ag}_3\text{PO}_4$  |
|              | $m3m$       | $\text{CaTiO}_3$ , Cu, W, diamond, $\text{NaCl}$ , $\text{CaF}_2$ , $\text{Al}_2\text{MgO}_4$ , $\text{As}_2\text{O}_3$ , $\text{CsCl}$ , $\text{Cu}_2\text{O}$ |

the particular Bravais lattice of the crystal system. This is followed by a slightly modified point-group symbol in the Hermann–Mauguin full notation. The point-group symbol indicates the crystal class (according to the 32 point groups) and of course, the crystal system. The point-group symbol is modified in the space-group notation in order to designate screw axes and glide planes when they occur. The space-group symbols of a few of the more symmetric crystals are listed in both Hermann–Mauguin and Schoenflies notation in Table 2-6.

The space groups for most substances are known and readily available [18, 21]. A description of just how a substance is assigned a space group on the basis of x-ray analysis is to be found in a book by M. J. Buerger [22].

Incidentally, the crystal class or point-group symmetry of any substance can be obtained from the Hermann–Mauguin space-group symbol for the substance by the following procedure: (1) Drop the capital letter of the group symbol; (2) change all other letters to *m*; and (3) drop all subscripts. For example, the space group for diamond shows that this substance belongs to the *m3m* class as follows:

$$F \frac{4_1}{d} \bar{3} \frac{2}{m} \rightarrow \frac{4}{m} \bar{3} \frac{2}{m} = m3m. \quad (2-19)$$

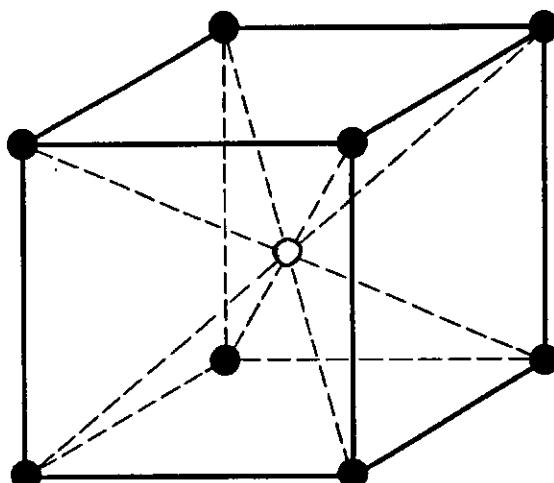
## 2-12 CRYSTAL STRUCTURES

Real crystals are systematically catalogued and their structure described according to *structure type* [20]. A few common structure types are listed in Table 2-7, where it is seen that each type is named after some characteristic substance. Alternatively, structures can be given a special symbol of their own and are described by space group, equivalent positions, etc. [20, 23]. Moreover, it should be noticed that the many and various structure types are distributed among 32 *crystal classes* according to point-group symmetry. We now discuss some important crystal structures beginning with the cubic system.

### CUBIC CRYSTAL STRUCTURES

We discuss in order the CsCl structure, body-centered cubic, face-centered cubic, NaCl, diamond, and CaF<sub>2</sub> structures.

Only one substance  $\alpha$ -polonium is known to crystallize into the *simple cubic* form of Fig. 2-1, a structure in which each atom is surrounded by six identical atoms. However, the Cs<sup>+</sup> ions in CsCl are on a simple cubic lattice as are the Cl ions. See Fig. 2-20. In this case, the two lattices



**FIGURE 2-20.** The cesium chloride structure.

are displaced so that each ion is at the body center of a cube of atoms of the other type. The conventional unit cell of this structure is chosen to resemble a body-centered cubic cell, and for CsCl, the edge of the cell, or lattice parameter, is  $a = 4.11 \times 10^{-8}$  cm. Such a cubic cell is not primitive but contains one molecule as a basis. If a cesium ion is at the origin, 0, 0, 0 ( $\text{Cs}^+$ ), a chlorine is at  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$  ( $\text{Cl}^-$ ). Various substances having the CsCl structure are listed in Table 2-8. The lattice parameters  $a$  in the tables which follow were taken from the *Handbook of Chemistry and Physics* [18] or from Pearson [23].

**TABLE 2-8.** Listing Some Substances Which Crystallize in the CsCl Structure. The Lattice Parameter  $a$  (in Angstroms) Is the Edge of the Conventional Cubic Cell

| Substance            | Lattice parameter<br>$a$ | Substance                      | Lattice parameter<br>$a$ |
|----------------------|--------------------------|--------------------------------|--------------------------|
| CsCl                 | 4.11 Å                   | $\text{NH}_4\text{Cl}$         | 3.87 Å                   |
| CsBr                 | 4.29                     | $\text{CuZn}$ ( $\beta$ brass) | 2.94                     |
| CsI                  | 4.56                     | $\text{AgMg}$                  | 3.28                     |
| TlCl                 | 3.84                     | $\text{LiHg}$                  | 3.29                     |
| TlBr                 | 3.97                     | $\text{AlNi}$                  | 2.88                     |
| TlI                  | 4.20                     | $\text{BeCu}$                  | 2.70                     |
| RbCl (high pressure) | 3.74                     |                                |                          |

**TABLE 2-9.** Substances Which Crystallize into a Body-centered Cubic Structure

|    | <i>a</i> |                | <i>a</i> |
|----|----------|----------------|----------|
| Li | 3.50 Å   | V              | 3.03 Å   |
| Na | 4.28     | Nb             | 3.29     |
| K  | 5.25     | Ta             | 3.29     |
| Rb | 5.69     | Cr             | 2.88     |
| Cs | 6.08     | Mo             | 3.14     |
| Ba | 5.01     | W              | 3.16     |
|    |          | Fe( $\alpha$ ) | 2.86     |

The conventional (nonprimitive) unit cell of the *body-centered cubic structure* is shown by dotted lines in Fig. 2-4. Such a cell contains two atoms of the same kind per unit cell at the positions  $0, 0, 0$  and  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ . The edge of the conventional cell is *a*, and each atom has eight nearest neighbors at a distance of  $\frac{1}{2}(3)^{1/2} a = 0.866 a$ . The alkali, refractory, and certain other metals are important examples as listed in Table 2-9.

Let us consider the *face-centered cubic structure* next. It can be seen from Fig. 2-4 that there are four atoms to each conventional cell. This is a close-packed structure and is the first of two ways of densely packing spheres. The other way of close packing spheres results in a hexagonal structure (hcp) discussed below. In the fcc structures each atom is surrounded by 12 nearest neighbors at a distance of  $\frac{1}{2}(2)^{1/2} a$  and six next-nearest neighbors at a distance of *a*. A list of fcc crystals includes the noble metals, copper, silver, and gold. The sodium chloride structure is a fcc lattice for each type of ion as shown in Fig. 1-1. This structure

**TABLE 2-10.** Substances Which Crystallize into the Face-centered Cubic Structures

|                | <i>a</i> |                | <i>a</i> |
|----------------|----------|----------------|----------|
| Cu             | 3.61 Å   | Th( $\alpha$ ) | 5.08 Å   |
| Ag             | 4.08     | Pb             | 4.94     |
| Au             | 4.07     | Fe( $\gamma$ ) | 3.64     |
| Sr( $\alpha$ ) | 6.07     | Co             | 3.54     |
| Al             | 4.04     | Ni ( $\beta$ ) | 3.52     |
| La( $\beta$ )  | 5.29     | Rh             | 3.80     |
| Ce             | 5.16     | Pd             | 3.88     |
| Sc             | 4.53     | Ir             | 3.82     |
| Yb             | 5.49     | Pt             | 3.92     |

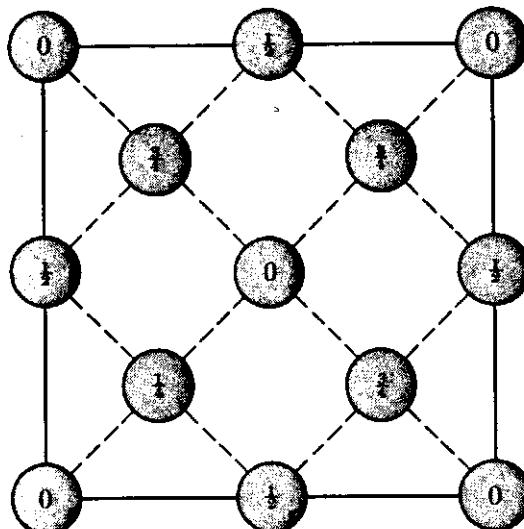
contains four molecules per conventional cubic cell. Each ion,  $\text{Na}^+$  or  $\text{Cl}^-$ , is surrounded by six ions of the opposite sign. The lattice parameter,  $a$ , given below is not the nearest neighbor distance between unlike ions but rather, as usual, the dimension of the cubic unit cell. All of the alkali halides except  $\text{CsCl}$ ,  $\text{CsBr}$ , and  $\text{CsI}$  crystallize in this structure. Examples are given in Table 2-11. One notices that the unit cell dimension,  $a$ , increases regularly from  $\text{Li}$  to  $\text{Rb}$ . Furthermore, the difference in  $a$ , between  $\text{NaF}$  and  $\text{KF}$  ( $\Delta a = 0.36 \text{ \AA}$ ),  $\text{NaCl}$  and  $\text{KCl}$  ( $0.33 \text{ \AA}$ ),  $\text{NaBr}$  and  $\text{KBr}$  ( $0.31 \text{ \AA}$ ),  $\text{NaI}$  and  $\text{KI}$  ( $0.30 \text{ \AA}$ ) are all nearly the same. Similar statements can be made concerning the different pairs of halogens. This leads one to assign a definite radius to an ion in an ionic crystal—the so-called Goldschmidt radii. The coordination number of the  $\text{NaCl}$  lattice is six, indicating less dense packing than in the case of  $\text{CsCl}$ , which has eight nearest neighbors. The  $\text{NaCl}$  structure seems to be favored for two ions of very much different size.

The *diamond lattice* is an important less densely packed cubic structure in which each atom is surrounded by only four nearest neighbors. This is favored by the valence bond and an electronic structure such as the one discussed in Chapter 1. The diamond structure can be thought of as two interpenetrating face-centered cubic lattices, in which one lattice is displaced relative to the other by one fourth of the cube diagonal. A conventional unit cell can be chosen as a face-centered cube of side  $a$  in which additional atoms have been placed along the diagonals. A total of eight atoms belongs to each unit cell of this type. Figure 2-21 shows a projection of the atoms of a unit cell onto a (100) face. The numbers

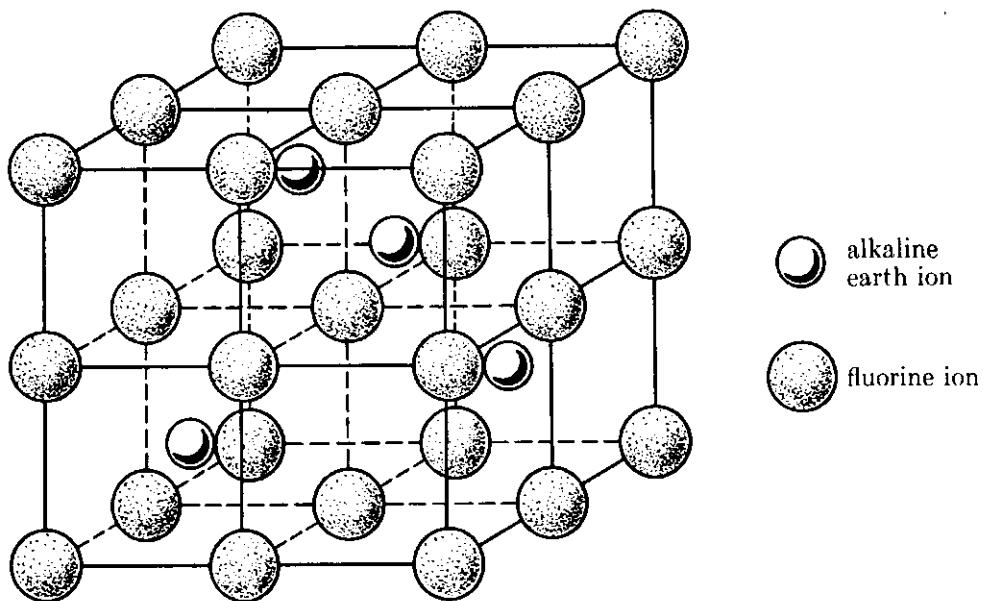
TABLE 2-11. Listing Substances Which Crystallize in the  $\text{NaCl}$  Structure

| Substance     | Lattice parameter $a$ | Substance                 | Lattice parameter $a$ |
|---------------|-----------------------|---------------------------|-----------------------|
| $\text{LiF}$  | 4.02 $\text{\AA}$     | $\text{LiI}$              | 6.00 $\text{\AA}$     |
| $\text{NaF}$  | 4.62                  | $\text{NaI}$              | 6.46                  |
| $\text{KF}$   | 5.33                  | $\text{KI}$               | 7.05                  |
| $\text{RbF}$  | 5.63                  | $\text{RbI}$              | 7.33                  |
| $\text{CsF}$  | 6.01                  | $\text{AgF}$              | 4.92                  |
| $\text{LiCl}$ | 5.14                  | $\text{AgCl}$             | 5.55                  |
| $\text{NaCl}$ | 5.63                  | $\text{AgBr}$             | 5.77                  |
| $\text{KCl}$  | 6.28                  | $\text{CaO}$              | 4.80                  |
| $\text{RbCl}$ | 6.54                  | $\text{MgO}$              | 4.20                  |
| $\text{LiBr}$ | 5.49                  | $\text{MnO}$              | 4.43                  |
| $\text{NaBr}$ | 5.94                  | $\text{NiO}$ (high temp.) | 4.195                 |
| $\text{KBr}$  | 6.59                  | $\text{PbS}$              | 5.92                  |
| $\text{RbBr}$ | 6.87                  | $\text{LiH}$              | 4.08                  |

indicate the distance below the plane for each atom in fractions of the cube edge. Important elements which crystallize in this structure are carbon, silicon, germanium, and grey tin. Some compounds, for example, the cubic form of ZnS, CdTe, etc., crystallize into a structure which resembles the diamond lattice except that nearest neighbors are of opposite kind. Such a crystal arrangement is known as the *zinc blende structure*.



**FIGURE 2-21.** *A projection of the atoms in the cubic cell of the diamond lattice onto a (100) face. Displacements of the atoms normal to the plane of the page are indicated in fractions of the cube edge.*

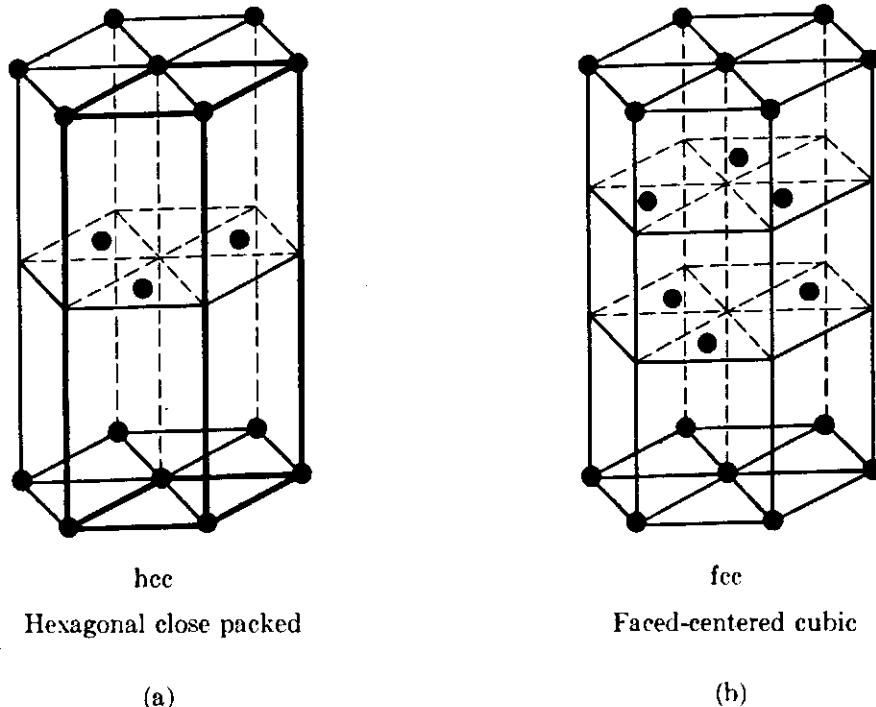


**FIGURE 2-22.** *The calcium fluoride lattice.*

Another important ionic crystal structure is the calcium fluoride structure shown in Fig. 2-22. The distance  $a$  between nearest fluorine ions in three alkaline earth fluorides is:  $\text{CaF}_2$ , 2.726 Å;  $\text{SrF}_2$ , 2.93 Å;  $\text{BaF}_2$ , 3.092 Å.

### HEXAGONAL CRYSTAL STRUCTURES

If one looks in the direction of a body diagonal of a face-centered cubic lattice, a hexagonal arrangement of lattice points is seen. You will recall that the fcc lattice is a close-packed lattice in which an atom is surrounded by 12 nearest neighbors. Another way of achieving 12 nearest neighbors, and therefore close packing, is found in the case of the *hexagonal close-packed structure*. This structure is formed by displacing a hexagonal net a distance  $a$ , except that a plane of atoms  $B$  is placed between the top and bottom hexagonal faces as shown in Fig. 2-23a. This arrangement results when spheres are close packed by placing in layers  $AB, AB, \dots$ , so to speak. Figure 2-23a is not a Bravais lattice but it can be thought of as the Bravais hexagonal  $P$  lattice (primitive cell outlined by solid lines) with a basis of two atoms at  $0, 0, 0$  and  $\frac{2}{3}, \frac{1}{3}, \frac{1}{2}$ . The face-centered cubic structure can be drawn to look very much like Fig. 2-23a, except that two planes, rotated 60° with respect to one another, are placed between the top and bottom hexagonal faces, as in Fig. 2-23b. The planes are stacked  $ABC, ABC, \dots$ , so to speak.



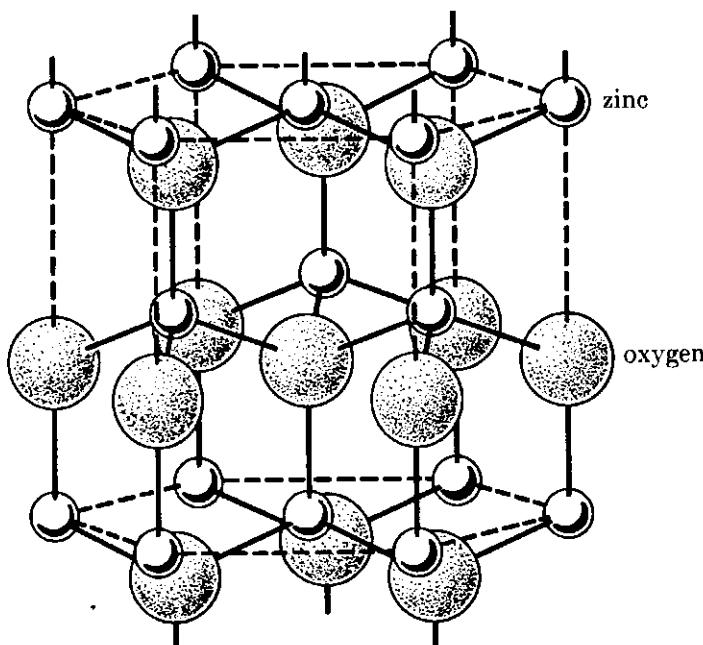
**FIGURE 2-23.** Showing a hexagonal close-packed lattice (a) and another way of drawing the face-centered cubic lattice (b).

**TABLE 2-12.** *The Lattice Dimension  $a$  and Axial Ratio  $c/a$  for Several Hexagonal Close-packed Metals*

| Substance      | $a$    | $c/a$ | Substance       | $a$    | $c/a$ |
|----------------|--------|-------|-----------------|--------|-------|
| Be             | 2.27 Å | 1.58  | Ti              | 2.95 Å | 1.60  |
| Mg             | 3.20   | 1.62  | Zr ( $\alpha$ ) | 3.22   | 1.59  |
| Ca ( $\beta$ ) | 3.98   | 1.64  | Re              | 2.76   | 1.62  |
| Zn             | 2.66   | 1.86  | Co ( $\alpha$ ) | 2.51   | 1.62  |
| Cd             | 2.97   | 1.89  |                 |        |       |

An axial ratio  $c/a = \frac{2}{3}(6)^{1/2} = 1.633$  results when identical spheres are hexagonal close packed. Several important metals have nearly this ratio as shown in Table 2-12.

When two different atoms are arranged on a hexagonal lattice so that nearest neighbors are atoms of opposite kind, the wurtzite structure results. Important examples of this structure include ZnO and the hexagonal forms of CdS and ZnS (which are usually more easily grown than the zinc blende modification). In these hexagonal crystals the atoms have tetrahedral coordination as in the zinc blende case. Examples are given in Table 2-13 and the lattice is shown in Fig. 2-24.



**FIGURE 2-24.** Zinc oxide and the hexagonal forms of CdS and ZnS have the wurtzite structure. (Courtesy of G. Heiland.)

**TABLE 2-13.** *The Lattice Dimension  $a$  and Axial Ratio  $c/a$  for Substances Which Crystallize in the Wurtzite Structure*

| Substance | $a$    | $c/a$ |
|-----------|--------|-------|
| ZnS (Hex) | 2.33 Å | 1.63  |
| CdS (Hex) | 2.52   | 1.62  |
| ZnO       | 3.25   | 1.60  |
| BeO       | 2.69   | 1.63  |
| MgTe      | 4.52   | 1.62  |

Note that several of the  $c/a$  ratios shown in Table 2-13 are very nearly the ideal value for hexagonal close packing (1.633), even though the stacking of alternate layers is not exactly as for spheres in contact. In fact, for most of the substances listed, different stacking sequences than  $AB$ ,  $AB, \dots$  can occur [23].

### MORE COMPLEX STRUCTURES

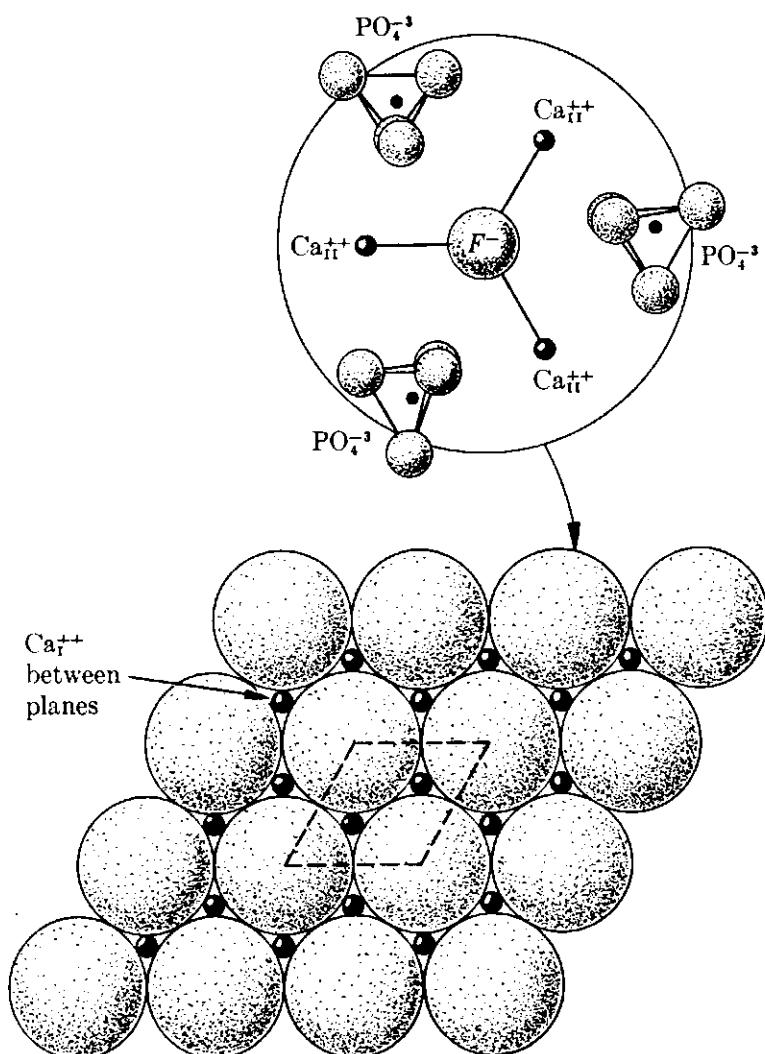
The reader should not be left with the impression that all crystal structures are as simple or as highly symmetric as those discussed above. Certainly the structure of crystals made up of large molecules can be exceedingly complex. Also, many minerals have a fairly involved structure. One relatively simple, but interesting case, is that of fluoro- or chloroapatite. Large single crystals of the apatites can now be made in the laboratory, and powdered material has found wide technological application in fluorescent lamps.

The empirical formula for fluoroapatite is  $\text{Ca}_5(\text{PO}_4)_3\text{F}$ . However, the calcium atoms exist in two nonequivalent sites designated  $\text{Ca}_I$  and  $\text{Ca}_{II}$ . All atoms except  $\text{Ca}_I$  and two oxygens in each  $\text{PO}_4$  group lie in the planes shown in Fig. 2-25. These are mirror planes and are repeated in a perpendicular direction except that every other plane has the atoms within each circle rotated about the fluoride axis by  $60^\circ$ . The  $\text{Ca}_I$  atoms are situated midway between the mirror planes, and two of the oxygen atoms in each phosphate lie on a line perpendicular to these planes. The unit cell contains 42 atoms and has a composition  $(\text{Ca}_I)_4 (\text{Ca}_{II})_6 (\text{PO}_4)_6\text{F}_2$ . Fluoroapatite has the space group  $C_{6h}^2$ .

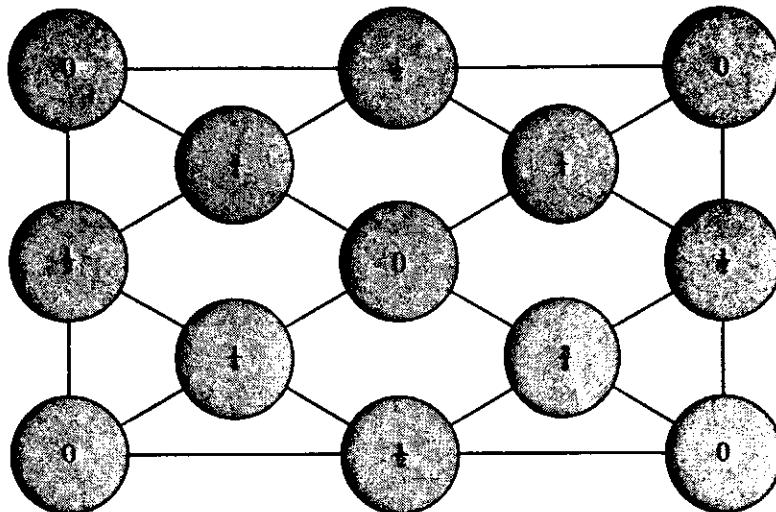
One need not turn to large molecules to illustrate intricacies of the crystalline state. The very heavy metals have several allotropic forms and sometimes less symmetric structure. For example, the  $\alpha$  phase of uranium, which is stable up to  $640^\circ\text{C}$ , is orthorhombic [26], with a space group  $Cmcm$  or  $D_{2h}^{17}$ . Plutonium has six allotropic forms. X-ray diffrac-

tion patterns of the lower temperature  $\alpha$  and  $\beta$  forms of Pu have been exceedingly difficult to interpret, although it is now known that the  $\alpha$  form (stable below 122°C) is monoclinic with space group  $P2/m$ . The structure of the  $\gamma$  phase (stable in the range 206 to 319°C) has been thoroughly described by Zachariasen and Ellinger [27]. These investigators found that the plutonium atoms are arranged on two interpenetrating face-centered lattices displaced relative to one another by one-fourth of the body diagonal. The positions of the eight atoms in the unit cell are shown in Fig. 2-26 and correspond to a space-group symmetry of  $Fddd$  or  $D_{2h}^{24}$ . The crystal structure of  $\gamma$  plutonium is unlike any other metal in that each atom is surrounded by ten neighbors, each at about the same distance.

We thus conclude our introduction to the subject of crystallography and proceed in the next chapter to a discussion of the diffraction of radiation by crystals.



**FIGURE 2-25.** A drawing which helps to describe the crystal structure of fluoroapatite, from R. K. Swank [25].



**FIGURE 2-26.** A projection of the atoms in the unit cell of  $\gamma$  plutonium upon the (001) face. (After Zachariasen and Ellinger [26].) Eight atoms are at the following positions in the unit cell:  $(0, 0, 0)$ ,  $(0, \frac{1}{2}, \frac{1}{2})$ ,  $(\frac{1}{2}, 0, \frac{1}{2})$ ,  $(\frac{1}{2}, \frac{1}{2}, 0)$ ,  $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ ,  $(\frac{3}{4}, \frac{3}{4}, \frac{1}{4})$ ,  $(\frac{3}{4}, \frac{1}{4}, \frac{3}{4})$ ,  $(\frac{1}{4}, \frac{3}{4}, \frac{3}{4})$ .

### PROBLEMS

**2-1.** Sodium chloride has a cubic unit cell (NaCl structure) with an edge of length  $a = 5.63 \times 10^{-8}$  cm. The atomic weight of sodium is 23 and the molecular weight of chlorine 71. Calculate the density of sodium chloride.

**2-2.** Consider an oblique lattice in two dimensions. Show by means of a drawing how the vector  $(2, 3)$  can be used as one of the basis vectors of the lattice. What second basis vector have you chosen? Demonstrate that the area of the parallelogram subtended by the vector  $(2, 3)$  and your chosen vector is equal to the area of the parallelogram subtended by the vectors  $(1, 0)$  and  $(0, 1)$ .

**2-3.** What is the inherent symmetry of the plane square lattice? Consider the rotation axes and mirror planes for this lattice and indicate these by means of symbols drawn at the appropriate places on a square.

**2-4.** As you know, there are only 14 Bravais or space lattices in all. Why are the following not included in the 14? (a) base-centered tetragonal, (b) face-centered tetragonal, (c) orthorhombic C plus a body-centered point.

**2-5.** Which planes of a cubic crystal contain three directions of different rotational symmetry? that is tetrad, triad, and diad axes? Give the angles between these directions in this plane.

**2-6.** The unit cell normally chosen for the body-centered cubic lattice has two atoms per cell and therefore is not a primitive cell. Wigner and Seitz proposed a cell which is primitive and still preserves the symmetry of the lattice. It is constructed by drawing connecting lines from one lattice point to all other lattice points and bisecting these by planes. This results in a polyhedron as

## CHAPTER 1

# MATERIALS PROPERTIES AND CRYSTAL LATTICES

### 1.1 INTRODUCTION.

The development of materials has played a crucial role in the growth of our present technological society. This book, while addressed primarily to students of engineering and materials science, is not about materials as such, but about the basic physics that determines what properties materials will have. Though its contents should be of interest to anyone concerned with materials, its main focus will be on electronic materials--the materials that go into integrated circuits and other solid-state devices. In view of this, a brief treatment of some elementary solid-state devices is also included.

The technology of electronic materials really began with Thomas A. Edison's quest for a practical incandescent lamp. This quest resolved itself into a search for a satisfactory filament material--one that would operate at a high temperature for a long time without burning out, and without consuming too much electrical energy. Edison finally developed a reasonably successful carbon-filament high-vacuum incandescent lamp in 1878. These bulbs, however, were fragile. Moreover, they darkened rapidly as a result of the deposition of carbon on the glass envelope, and suffered from premature burnout. Tungsten was known to be a potentially superior filament material in view of its low vapor pressure at high temperatures, but turned out to be almost impossible to form into wires and filaments. It took over 20 years to develop the technology of refining and forming tungsten, but at last the problems were overcome, and much better incandescent lamps--the kind we use today--were developed.

The development of tungsten filaments, and the related art of sealing electrodes into evacuated glass envelopes soon gave birth to high-vacuum diode rectifiers, and finally, in 1906, led to de Forest's invention of the vacuum triode, a device which could be used as an amplifier or oscillator, and which soon brought forth the

branch of technology we now know as *electronics*. Edison himself had been (in 1886) the first to observe the curious unidirectional currents that could be made to flow in the apparently empty space between a hot filament and a cathode sealed in a high vacuum. Indeed, had he exhibited the slightest interest in the origin of this effect, he might well have become the discoverer of the electron. Unfortunately, however, he was obsessed with the development of incandescent lighting, and the electron was not identified until 1897 by J. J. Thomson, a Cambridge physics professor. Thomson was awarded the 1906 Nobel Prize in physics for the discovery of the electron.

By 1947, a large communications and consumer electronics industry had been spawned by the technology of vacuum-tube electronics. Radio transmitters and receivers, television sets, disc and tape recording and playback equipment, and radar and other defense systems all utilized vacuum tubes, despite inherent problems related to size, filament power dissipation, fragility, and limited service life. These problems stimulated scientific research in such subjects as electron physics, gas discharges, thermionic emission from metals and oxide-coated cathodes, secondary electron emission, photoemission, etc. During the first half of the 20th Century, the behavior of electrons in metals and other crystals also began to be studied in a systematic way, and by about 1940 a discipline called solid-state physics had achieved legitimacy as a subfield of modern physics.

The earliest application of solid-state electronics was in crystal detectors of radiofrequency signals in early radio receivers. These devices were simply rectifiers consisting of a fine metallic point--usually referred to as a "cat whisker"--in contact with a crystalline semiconductor such as galena, i.e., lead sulfide. The cat whisker had to be positioned carefully in the vicinity of a "hot spot" on the crystal to make the device work properly. Actually, nobody understood exactly how these devices operated, but they were nevertheless in fairly widespread use in simple receivers (known as "crystal sets") during the first two decades of this century. During World War II, semiconductors came to be better understood, and point contact rectifiers, now using crystals of germanium and silicon, were designed for use at microwave frequencies as radar detectors.

It soon became apparent that it should be possible to utilize electron currents in semiconductor crystals to do all the useful tasks that could be accomplished by vacuum tubes. Soon after World War II, physicists began an intense study of the properties of these materials with the objective of fabricating a solid-state triode. This objective was realized with the invention of the transistor by Shockley, Bardeen and Brattain, at Bell Laboratories in December 1947. The invention of this device was a direct outgrowth of fundamental research in semiconductor physics.

Since then, the growth of electronics has been associated almost exclusively with the development of solid-state materials, solid-state devices, and integrated circuits fabricated from solid-state elements. If you wish to pursue the study of electronics, electronic materials, electron devices, or for that matter materials science in general, you must therefore begin by learning the fundamentals of solid-state physics. You will also have to learn the elements of *quantum mechanics*, because the laws of classical physics are inadequate to describe the behavior of matter on the atomic scale. In this book, that subject is presented as an integral part of the text, and you will learn it as you go along. In fact, the road begins at this point.

## 1.2 SOLIDS, LIQUIDS, AND GASES

Most of the materials we encounter in everyday life can be classified as solids, liquids, or gases. In gases, the molecules are relatively far apart, and the forces between them are not strong enough to bind the atoms or molecules tightly to each other. There are therefore comparatively few molecules per unit volume, and the density of the substance is relatively low. A gram mole of an ideal gas, for example, occupies a volume of 22.4 liters at 0°C and one atmosphere pressure. In gases, the positive kinetic energy of the molecules is greater than their mutual potential energy of interaction, which will be negative if the intermolecular forces are attractive, as they ordinarily are. This means that the system has net kinetic energy, and that if it is unconfined, the molecules will escape to infinity. The situation is like that of a rocket given an initial upward velocity greater than the escape velocity associated with the earth's gravitational field at the launch site. Such an object has more positive kinetic energy than negative gravitational potential energy, and it will escape to infinity rather than falling back to the earth's surface. In a gas, the molecular velocities, on the average, are greater than the "escape velocity" associated with the intermolecular forces of attraction. In an *ideal* gas, the intermolecular forces are negligible, and the molecules behave like particles that are free except for occasional elastic collisions with each other, and with the walls of the container.

An ideal crystalline solid is the exact opposite of an ideal gas, in the sense that the atoms are tightly bound to one another in a regular periodic lattice by very strong attractive forces, as illustrated in Figure 1.1. Within the crystal, neighboring atoms are so close together that their external electron distributions are starting to overlap and interact; in effect, the atoms are in contact with one another. In this condensed state, the density of matter is much greater than that of gases at room temperature and atmospheric pressure. A gram mole of a crystalline solid typically occupies a volume of only 10 to 100 milliliters, and the atoms are only 2 Ångströms or so ( $1\text{\AA} = 10^{-10}\text{m}$ ) apart. Under these circumstances, the energy of the system is mostly negative potential energy associated with the attractive forces between individual atoms. Though the atoms may have some thermal kinetic energy, this is only a small part of their total energy. The total energy of the system is therefore negative, which is simply another way of saying that the particles remain bound to well-defined equilibrium positions. The only effect of the thermal kinetic energy the particles may have is to make them oscillate about their equilibrium positions. In an *ideal* crystal these oscillations are harmonic motions whose amplitude is much smaller than the interatomic spacing. Since the ideal crystal is so simple physically, its properties are also easy to calculate. Partially for this reason, but also because the ideal crystal model is quite adequate for many purposes, we shall find it useful as the basis of much of our forthcoming work.

It is important, however, to understand that many solids do not conform to the ideal crystal model described above. First of all, lattice imperfections such as lattice vacancies and extra interstitial atoms may be present, along with other defects in the regular periodic structure of the crystal. In many cases, there may be large regions of nearly perfect crystalline order, each having a different lattice orientation, separated by thin, highly disordered boundary regions. Such substances are referred

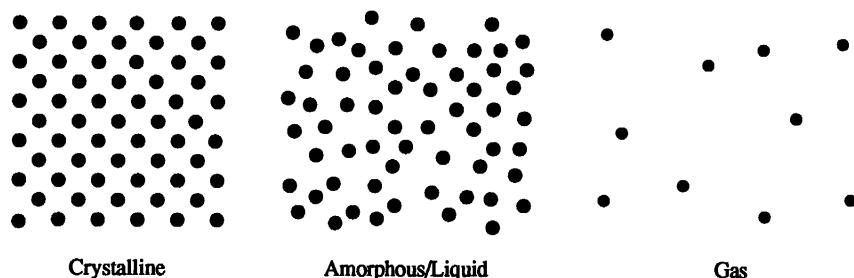


Figure 1.1. Two-Dimensional schematic representation of crystalline solids, amorphous materials or liquids, and gases. In gases, the atoms can be much further apart than shown above.

to as *polycrystalline* materials. Ordinary metals, in the "as prepared" state, for example, are usually polycrystalline. Fortunately, the ideal crystal model provides a description of these materials that is satisfactory for many purposes. In certain other solid materials, the atoms are arranged more or less randomly. The resulting structure has none, or very little, of the long-range regularity of an ideal crystal. Materials of this type are called *amorphous* substances. Glass is a typical example of an amorphous material. Sometimes amorphous solids can be regarded as supercooled liquids of enormous viscosity. In many cases, the ideal crystal model still suffices to give a rough, though useful, description of their properties. Amorphous materials are important in electronics and materials engineering, though we shall not attempt to treat them in detail in this book.

Liquids resemble solids in that their density and interatomic spacing are much closer to those of crystalline substances than gases. In liquids, however, there is none of the geometric regularity of the crystalline solid, the atoms or molecules being randomly arranged, as in an amorphous solid. To attain the liquid state, however, you must raise the temperature of a solid until it melts. In doing this, one increases the kinetic energy of the atoms, which in the crystalline state is purely vibrational. As the temperature rises, the amplitude of atomic vibrations in the crystal increases until it finally approaches the interatomic spacing. At this point, the atoms attain enough kinetic energy to break loose from their former positions of equilibrium and move more or less freely past one another. They are still bound to one another in a dense, compact phase, but they now have translational as well as vibrational kinetic energy. In this state, atoms can move around more or less freely within the substance, even though they cannot generally escape to infinity. The substance has now melted and become a liquid. Solids and liquids are often collectively referred to as *condensed matter*, and what used to be referred to as solid-state physics is now more frequently called condensed-matter physics in view of the fact that solids and liquids are both condensed phases characterized by small interatomic distances and high density. The fact that this book retains the earlier designation in its title merely reflects the fact that it is largely concerned with crystalline substances.

Obviously, you can convert a crystalline solid first to a liquid and finally to a gas or vapor, by progressively raising the temperature. At a given temperature, for example room temperature, different substances may exist in any of these three possible states. Under these conditions, what determines whether any given material is solid, liquid, or gas, is the *strength* of the attractive forces between atoms or molecules. In gases, these forces are weak, in crystalline solids, they are strong. What

determines how strong they are in any given substance is a complex question, which can be answered fully only in the context of quantum mechanics. Indeed, the answer to this question is one of the main things you can learn by studying solid-state physics. It is premature, however, to try to answer it now.

In addition to crystalline materials, we shall have to spend some time and effort studying the properties of ideal free-particle gases. This may seem surprising, because gases are physically at the opposite extreme from crystalline materials. However, the electrical properties of conducting substances can be understood only by observing that the valence electrons of their atoms are essentially free within the crystal. These electrons can be visualized as forming a free-particle gas within the substance, a gas which is confined by the external surfaces of the crystal. In order to understand the electrical behavior of conducting materials, therefore, it is necessary to study the properties of this "free-electron gas". These properties, as we shall see later, are similar in many ways to those of ordinary ideal monatomic gases.

### 1.3 LATTICES, UNIT CELLS, AND CRYSTAL SYMMETRY

Real crystal lattices are, of course, three-dimensional structures. The simplest of these is the lattice of points having integer coördinates  $(h, k, l)$  in an orthogonal cartesian coördinate system. Such a system can be thought of as being composed of cubic cells as basic structural units. This lattice is illustrated in Figure 1.2; it is called a simple cubic lattice. Three-dimensional structures are difficult to portray on paper, and are also somewhat complicated geometrically. Frequently, however, their basic geometry, and also the basic physics connected with them, can be adequately described with reference to two-dimensional, or even one-dimensional models, which are much simpler to portray, to visualize, and to analyze mathematically. There are situations in which this kind of simplification is not possible, but when it is valid, it is extremely helpful; in this book it will be frequently employed.

Figure 1.2(b) illustrates a two-dimensional crystal lattice which can be used to portray the basic geometry of ideal crystals. The parallelogram ABCD may be chosen as a *unit cell* of the crystal; the cell itself is in turn determined by the *basis vectors*  $\mathbf{a}$  and  $\mathbf{b}$ . It is clear from the diagram that the entire crystal can be mapped out by translating the unit cell along the  $\mathbf{a}$ - and  $\mathbf{b}$ -directions by integral multiples of those vectors. Thus, any lattice point in the crystal is located with respect to an origin at A by a vector  $\mathbf{R}$  of the form

$$\mathbf{R} = h\mathbf{a} + k\mathbf{b}, \quad (1.3-1)$$

where  $h$  and  $k$  are integers. Moreover, in an infinite lattice, a point P, located with respect to A by vector  $\mathbf{r}_P$ , is carried by the transformation  $\mathbf{r}_Q = \mathbf{r}_P + \mathbf{R}$ , where  $\mathbf{R}$  is any vector of the form (1.3-1), into a point Q whose surroundings are geometrically identical in all respects to those of P. This property, called *translational invariance* can be regarded as defining geometrically what is meant by a crystal lattice. It is obvious that this procedure can be extended to define unit cells and basis vectors in three-dimensional lattices. Translational invariance is illustrated in Figure 1.2(b),

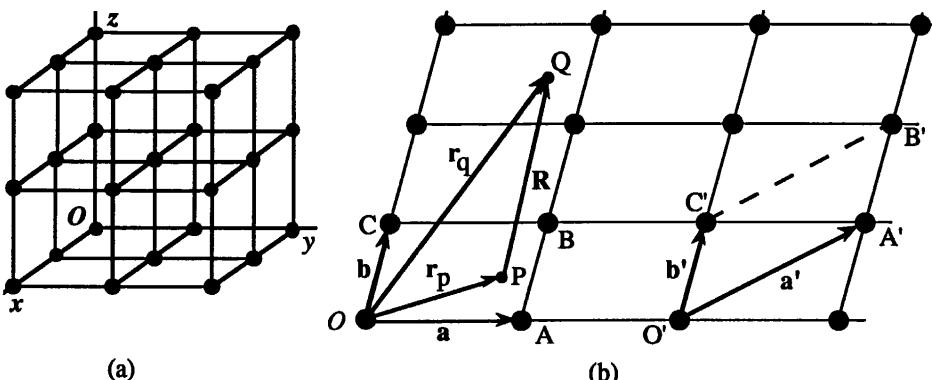


Figure 1.2 (a) Cubic lattice cells generated by points in an orthogonal cartesian coördinate system whose coördinates are all integers. (b) Two-dimensional unit cells and basis vectors.

where the lattice vector  $\mathbf{R}$  (equal to  $0\mathbf{a} + 2\mathbf{b}$  in this instance), translates the point  $P$  to a new location  $Q$ . It is evident that the physical surroundings of  $P$  and  $Q$  are the same, and that there is a point with these same surroundings in every unit cell of the crystal. We are thus led to suggest the following definitions:

**Unit Cell:** A region of the crystal defined by three vectors,  $\mathbf{a}$ ,  $\mathbf{b}$ , and  $\mathbf{c}$ , which, when translated by a vector displacement consisting of a sum of integral multiples of these vectors, reproduces a similar region of the crystal.

**Basis Vectors:** A set of linearly independent vectors  $\mathbf{a}$ ,  $\mathbf{b}$ , and  $\mathbf{c}$  which can be used to define a unit cell.

**Primitive Unit Cell:** The smallest unit cell, in volume, that can be defined for a given lattice.

**Primitive Basis Vectors:** A set of linearly independent vectors that can be used to define a primitive unit cell.

It should be observed that unit cells can be defined in more than one way. For example, in Figure 1.2(b), the most obvious--and sensible--choice of a unit cell is  $OABC$ . However, the larger cell  $OO'C'C$  could also be used inasmuch as it will map out the whole crystal by appropriate translations defined by its set of basis vectors  $OO'$  and  $OC$ . This cell is non-primitive, since it is larger than the primitive cell  $OABC$ . The cell  $O'A'B'C'$ , defined by the basis vectors  $a'$  and  $b'$  might also be used. In this case, the unit cell can be seen to be equal in area to  $OABC$ ; it is therefore also a primitive unit cell. It is also important to remember that the basis vectors of a crystal lattice are not unit vectors. Instead, they are dimensional vectors whose magnitudes are those of the interatomic spacing along the crystal axes. Moreover, it should be apparent that the lattice points of a three-dimensional lattice are described by a lattice vector  $\mathbf{R}$  of the form

$$\mathbf{R} = h\mathbf{a} + k\mathbf{b} + l\mathbf{c}, \quad (1.3 - 2)$$

where  $h$ ,  $k$ , and  $l$  are integers. Finally, the property of translational invariance is also clearly valid in three dimensional crystals.

#### 1.4 CRYSTAL STRUCTURES IN THREE DIMENSIONS

The study of crystal symmetry and general three-dimensional crystal geometry is full of subtle and complex details. Indeed, the subject constitutes an entire subfield of solid-state physics called *crystallography*, to which many scientists have devoted their entire lives. It is important to know some of the basic facts and terminology of this subject to develop an understanding of the physical properties of crystalline materials, but fortunately, a brief overview is all that is needed at the outset. We shall therefore present only a very elementary treatment of this subject. You should understand this clearly, and not be put off by the fact that our discussion leaves many seemingly important questions unanswered. The answers to these questions are simply a matter for more advanced study, and involve issues peripheral to the primary objectives of this text. Also, you will be presented with some results that are merely stated, with no attempt at derivation, nor even detailed explanation in some cases. Again, the facts are all you need to know at this point, the complex and difficult arguments for their validity being irrelevant to our present objectives.

Initially, one can show--with considerable difficulty--that there are exactly 14 ways of arranging points in space such that the physical surroundings of each lattice point is the same. This is the same as saying that if your crystal is made up of spherically symmetric atoms (whose symmetry properties are the same as those of point objects) you can draw only 14 different unit cells. These 14 arrangements are referred to as *Bravais lattices*, and are illustrated in Figure 1.3. They can be further subdivided into seven *crystal systems*, each of which is characterized by a unique symmetry property, such as invariance under rotation through given angles about certain axes, or under inversion, an operation in which a vector  $\mathbf{r}$  from the cell origin to a lattice point is replaced by  $-\mathbf{r}$ . These crystal systems are listed, along with their unit cell descriptors and characteristic symmetry elements, below Figure 1.4, which illustrates the notation pertaining to the size and shape of the unit cell.

If only spherically symmetric atoms were involved, there would be only 14 possible crystal structures. In general, however, lattice points may represent not only a single atom, but a group of atoms, or an entire molecule. The overall symmetry properties of a crystal will thus generally depend not only upon the symmetries of the Bravais lattice itself, but also on the symmetry properties of the atom or group of atoms at the lattice sites with reference to the lattice points themselves. When this added complication is taken into account, the number of possible crystal structures increases to 230. One now begins to see why crystallography is such a complicated business.

We are fortunate, however, that most important electronics materials, as well as many metals and alloys form crystals whose unit cells have mutually orthogonal axes. Indeed, most of these materials have cubic unit cells. This simplifies their geometry significantly, and allows those whose interest is confined to substances such as these to proceed without getting much further concerned with problems  
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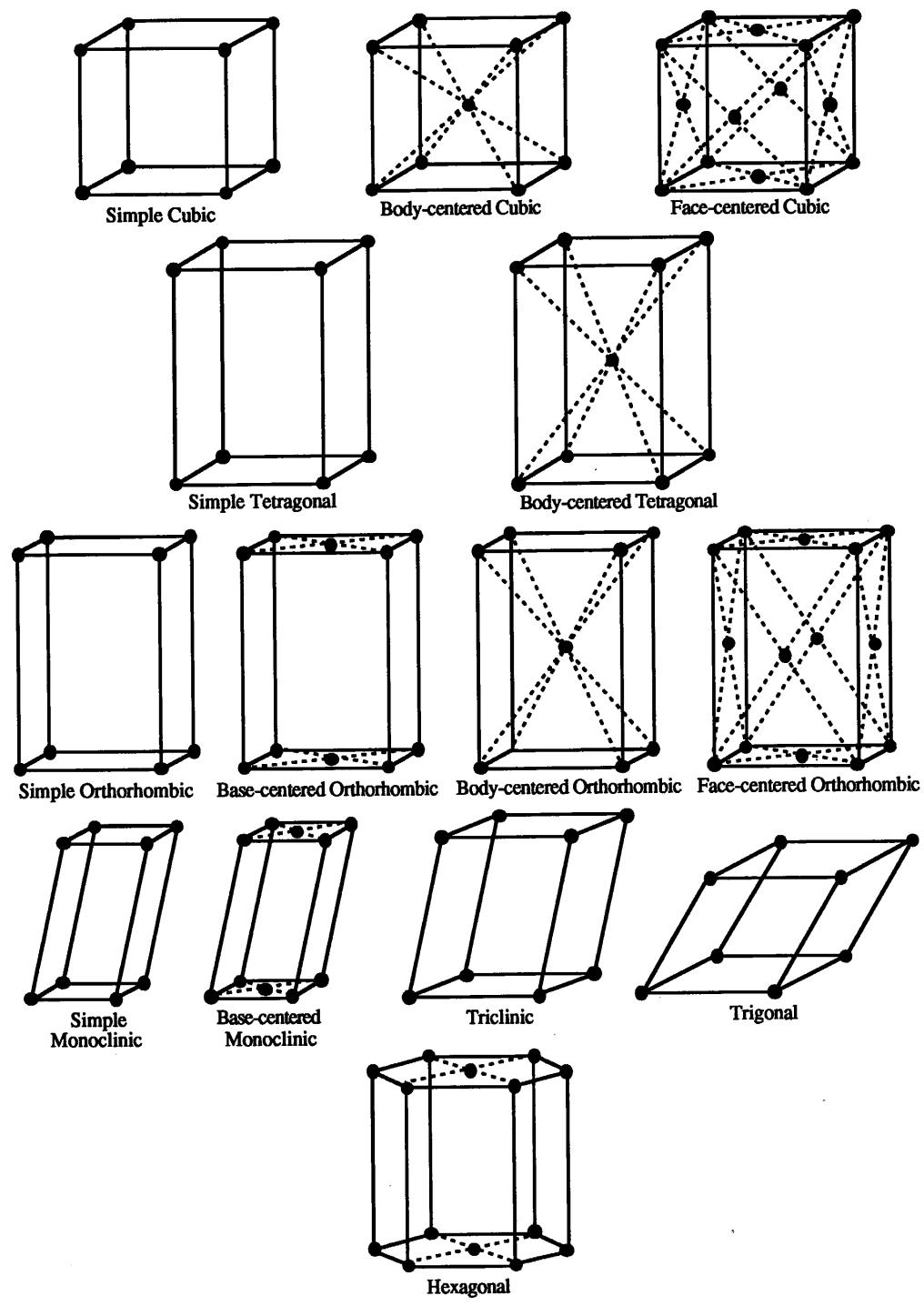


Figure 1.3 The 14 Bravais lattices

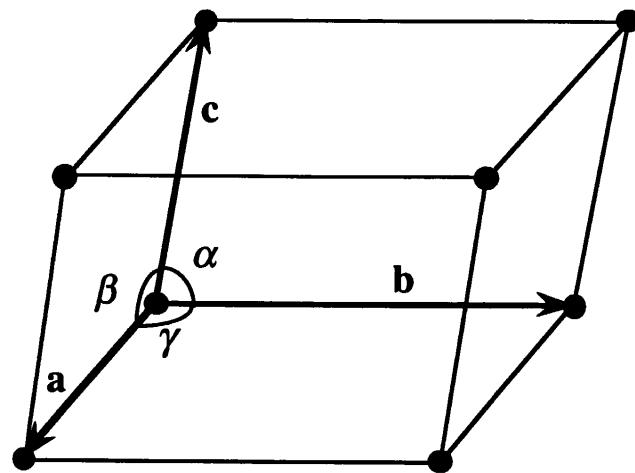


Figure 1.4. Notation for dimensions and angles within the unit cell of a crystal.

### THE SEVEN CRYSTAL SYSTEMS

| System       | Unique Symmetry Element                        | Bravais Lattice   | Unit Cell   |
|--------------|--|---|---|
| Triclinic    | None   | Simple  | $a \neq b \neq c$<br>$\alpha \neq \beta \neq \gamma \neq 90^\circ$    |
| Monoclinic   | One 2-fold rotation axis*                      | Simple<br>Base-centered                                   | $a \neq b \neq c$<br>$\alpha = \beta = 90^\circ \neq \gamma$          |
| Orthorhombic | Three mutually orthogonal 2-fold rotation axes | Simple<br>Base-centered<br>Body-centered<br>Face-centered | $a \neq b \neq c$<br>$\alpha = \beta = \gamma = 90^\circ$             |
| Tetragonal   | One 4-fold rotation axis                       | Simple<br>Body-centered                                   | $a = b \neq c$<br>$\alpha = \beta = \gamma = 90^\circ$                |
| Cubic        | Four 3-fold rotation axes (cube diagonals)     | Simple<br>Body-centered<br>Face-centered                  | $a = b = c$<br>$\alpha = \beta = \gamma = 90^\circ$                   |
| Hexagonal    | One 6-fold rotation axis                       | Simple  | $a = b \neq c$<br>$\alpha = \beta = 90^\circ$<br>$\gamma = 120^\circ$ |
| Trigonal     | One 3-fold rotation axis                       | Simple  | $a = b = c$<br>$\alpha = \beta = \gamma \neq 90^\circ$                |

\* The term  $n$ -fold rotation axis refers to invariance under a rotation of  $360/n$  degrees about some specific axis.

related to more complex structures. We shall concentrate, therefore, on a few simple but important structures.

There are three lattices having cubic symmetry, the simple cubic (s.c.), body-centered cubic (b.c.c.), and face-centered (f.c.c.) structures. In the case of the simple cubic structure, the cubic unit cell shown in Figure 1.3 is also a primitive cell, since there is no smaller cell definable. In this structure there is one atom per unit cell, a fact that can be understood by observing that there are 8 corner atoms shared equally between eight adjoining cells at each lattice point. There is therefore  $8(1/8) = 1$  atom per cell. In the cubic cell of the body-centered structure, however, there are two atoms, the 8 corner atoms yielding one atom as in the s.c. case, and a central atom belonging exclusively to the cell accounting for the other. In the face-centered structure, there are four atoms per cubic cell; 8 corner atoms, which contribute one atom to the cell, and 6 face-center atoms shared between two adjoining cells, which contribute  $6(1/2)$  or 3 additional atoms. Since simple structures made up of a single atomic species ordinarily have only one atom per primitive cell, one is led to suspect that the b.c.c. and f.c.c. cells are not primitive, and that these structures can be defined by a smaller structural unit. This turns out to be true; the primitive cells for these two lattices are illustrated in Figure 1.5. Each of these primitive cells contains only one atom.

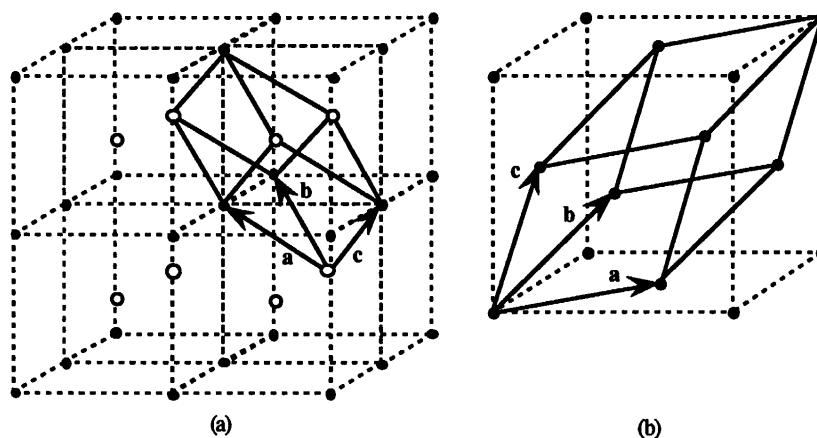


Figure 1.5 Primitive unit cells for (a) the body-centered and (b) the face-centered cubic structures. In (a) the atoms are all the same despite the fact that those at the centers of the cells are highlighted to clarify spatial relationships.

For most purposes it is more convenient to use the larger cubic cell, in view of the simplicity of coördinate geometry in orthogonal systems. Occasionally, however, we shall encounter applications where it is essential to use the primitive cell. We shall identify these situations whenever they occur. The f.c.c. primitive cell can be readily identified as a trigonal unit cell in which the angles  $\alpha$ ,  $\beta$ , and  $\gamma$  are all  $60^\circ$ . For this particular angle the trigonal lattice exhibits cubic symmetry, and reduces to the f.c.c.

In the simple cubic lattice, each atom is clearly surrounded by 6 nearest neighbors. The number of nearest neighbor atoms is referred to as the *coördination number* of the structure. Simple cubic thus has a coördination number of 6. The

b.c.c. structure is easily seen to have a coördination number of 8, while for f.c.c., the coördination number is 12, the nearest neighbor distance being along the face diagonals. Structures with few nearest neighbors are relatively "open" in character, while those in which each atom is surrounded by many neighboring atoms are comparatively densely packed. The coördination number is therefore directly related to the density with which atoms are arranged within the crystal. The largest possible coördination number is 12; structures in which each atom is surrounded by 12 nearest neighbors are therefore referred to as *close-packed* configurations. The f.c.c. lattice is the most common example of such a structure.

Within the unit cell, the positions occupied by atoms, and other points also, are often described by cell coördinates defined as fractional parts of the basis vectors  $\mathbf{a}$ ,  $\mathbf{b}$ , and  $\mathbf{c}$ . For example, the body-center atom in the b.c.c. cubic cell would have cell coördinates  $(1/2, 1/2, 1/2)$ , while the topmost face-center atom in Figure 1.5(b) would have cell coördinates  $(1/2, 1/2, 1)$ .

When equal spheres are packed into a container, the densest packing is obtained by first inserting a bottom layer in which each sphere is surrounded by a hexagonal array of 6 nearest neighbors. On top of this, one may put a similar layer, using the triangularly disposed interstices between spheres in the bottom layer to hold the spheres in the upper one. It is evident that in such an arrangement, each sphere in the bottom layer will be in contact with three spheres in the layer above. In the interior of a close-packed array of spheres, therefore, each sphere is in contact with 12 nearest neighbors; six in its own layer, three in the layer above, and three in the layer below.

There are two different structures having this property of close packing, in which the coördination number is 12, and they differ only in the manner in which the close packed layers are stacked upon one another. In the first, the spheres in the third layer are positioned directly above those in the first, those in the fourth are directly above those in the second, etc., resulting in a layer stacking that can be designated as ABABAB.... This structure turns out to have hexagonal symmetry, and is referred to as *hexagonal close-packed*. When you start the third layer of the packed array, however, you find that instead of positioning the third-layer spheres directly above those in the first layer, you can place them in another set of sites, in which they are not directly above either first-layer or second-layer spheres. Designating these sites as C-positions, one can then form the repetitive sequence ABCABCABC... as an alternate stacking pattern. In this structure, layers 1, 4, 7..., 2, 5, 8..., and 3, 6, 9... are directly above one another. This arrangement turns out to be the face-centered cubic lattice, a structure we have already identified as close-packed. In f.c.c. the close-packed layers lie in planes normal to the *diagonal* of the cubic f.c.c. unit cell. These structures are illustrated in Figure 1.6.

The simple cubic lattice is the simplest structure nature has provided for the formation of crystals. One might therefore expect that many substances crystallize in this manner. In fact, the reverse is true; there are only a few substances that form simple cubic lattices. The reason is that the attractive forces that act between the atoms or molecules of most substances make it energetically favorable for the atoms to be closer together than they would be in the s.c. lattice, whose coördination number is only 6. They therefore tend to assume more densely-packed structures, such as b.c.c. and f.c.c. On the other hand, if density of packing were the only factor at work, there would be only two possible structures--the ones illustrated in Figure 1.6. In

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reality, though density of packing is often significant, other factors can also be important.

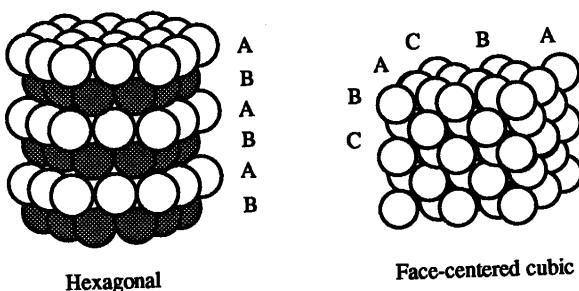


Figure 1.6 Hexagonal and cubic close-packed structures

The diamond lattice, illustrated in Figure 1.7(a), provides an excellent example of this ambivalence. Silicon and germanium, as well as diamond, crystallize in this structure. It is a very "open" lattice, with a coördination number of only 4. Despite this fact, diamond, silicon, and germanium are hard, strong, stable materials which exhibit little tendency to undergo phase changes into more densely packed crystalline structures. The reason is simple; carbon atoms have a strong tendency to form covalent electron-pair bonds with one another. These electron-pair carbon-to-carbon linkages are, in fact, what hold most organic molecules together. The tetravalent character of the carbon atom imparts a natural tetrahedral geometry to the covalent bonds that surround each atom. This tetrahedral geometry is perfectly accommodated by the diamond structure. Indeed, the tetrahedral units of which it is composed are its most obvious geometrical feature. So despite the low density of packing, carbon crystallizes in this form, as do its sister elements silicon and germanium, which like carbon occupy column IV of the periodic table. It is of course true that there exists another crystalline form of carbon, but graphite is no more densely packed than diamond, and valency is also the predominant mechanism in its structural makeup.

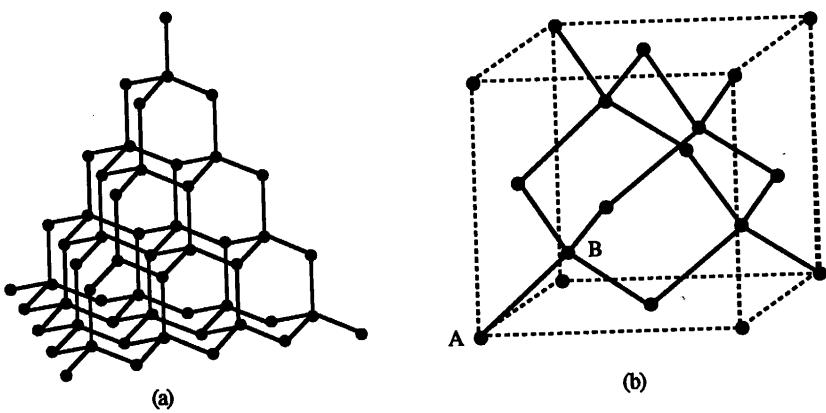


Figure 1.7 (a) The diamond structure (b) The diamond structure fitted into a cubic unit cell.

The diamond lattice turns out to have cubic symmetry, a fact not at all apparent from the diagram shown in Figure 1.7(a). In this diagram, the electron-pair bonds are shown as solid lines connecting nearest-neighbor atoms. Figure 1.7(b) illustrates how this structure can be fitted into a cubic unit cell. It can be regarded as two interpenetrating f.c.c. lattices, one based on an origin at A, the other based on B. Another way of looking at it is as a b.c.c. lattice with many of its atom sites vacant. The diamond lattice is not a Bravais lattice, since it can be regarded as an f.c.c. structure having the two-atom group AB on the lattice points rather than a single atom at each point. The bond length AB in the diamond structure is equal to one-quarter of the cubic cell diagonal.

The so-called III-V intermetallic compounds are also important electronic materials. They are composed of equal numbers of atoms from columns III and V of the periodic table, and thus have an *average* of four valence electrons per atom. They therefore satisfy the valency requirements of a tetrahedrally coördinated structure, and in fact crystallize in a lattice very similar to the diamond structure. The arrangement of atoms in this structure is identical to that of the diamond structure, the column III atoms occupying the f.c.c. sites based on A, the column V atoms occupying B sites. In this so-called *zinblende* structure, the two different atomic species are on alternate neighboring diamond-lattice sites, each column III atom being surrounded by four tetrahedrally disposed column V atoms (and vice-versa) so as to satisfy the bonding requirements of four covalent electron-pair bonds, which need a total of eight electrons. Gallium arsenide (GaAs) is the most important substance having this configuration, though other III-V semiconductors such as InSb, InP, and GaP have been used in electronic applications.

The structures of two simple ionic salts, NaCl and CsCl are illustrated in Figure 1.8. The NaCl structure has alternating sodium and chlorine atoms at the lattice points of a simple cubic lattice. The structure can also be viewed as two interpenetrating f.c.c. lattices, one of which is composed entirely of sodium atoms, the other

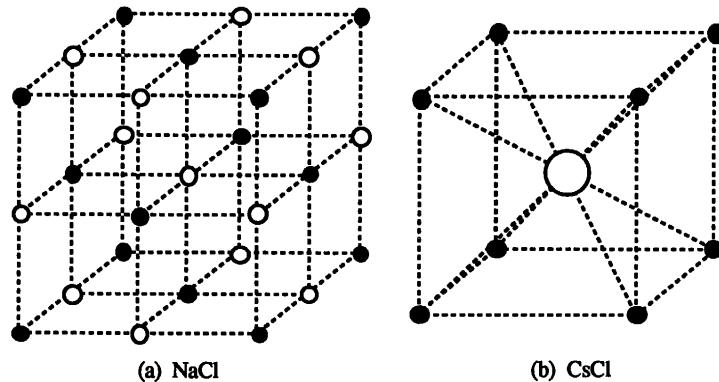


Figure 1.8 The sodium chloride and cesium chloride structures.

entirely of chlorine atoms. The CsCl structure is essentially body-centered, with cesium atoms at body centers and sodium at cube corner sites. Many other ionic crystals are found to crystallize in one or the other of these configurations.

### 1.5 CRYSTAL PLANES, DIRECTIONS, AND MILLER INDICES

If you look at a three-dimensional crystal model, or at illustrations such as Figures 1.2(a), 1.3, 1.5, 1.6 1.7, or 1.8(a), you will notice that there are certain clearly defined planes, densely populated with atoms, that run through the crystal in various directions. The two-dimensional line traces of these planes in the plane of the page are also easily seen in the leftmost drawing of Figure 1.1, particularly when the figure is viewed from a small angle to the page and the page rotated about a vertical axis to display the structure from various directions. The atoms lying in the plane of the cube faces of cubic unit cells render these crystal planes highly visible, but other prominent planes making various angles with the cell faces can also be observed. For example, in cubic cells, atoms lying in planes normal to face diagonals and to the cell diagonals are also clearly visible. There are other less prominent families of planes, making odd angles to the cell faces, and less densely populated with atoms, which can also be distinguished. Indeed, there is a whole hierarchy of planes of this sort within the crystal lattice.

These sets of planes are involved in a number of important physical processes that occur in crystals. For example, the diffraction of X-rays is an important tool for chemical analysis and determination of the lattice structure of crystalline solids. X-ray diffraction, however, can be visualized as involving reflection of X-rays from various sets of crystal planes, in such a way that outgoing beams reflected from adjacent planes of any such set interfere constructively. This process, which we shall consider in detail in the next chapter, is referred to as *Bragg reflection*. Bragg reflection is also involved in the diffraction of electrons and neutrons by crystals. In analyzing diffraction phenomena, the orientation and spacing of the families of crystal planes must obviously play an important part. It is of some interest, therefore to study the geometry of crystal planes within the lattice.

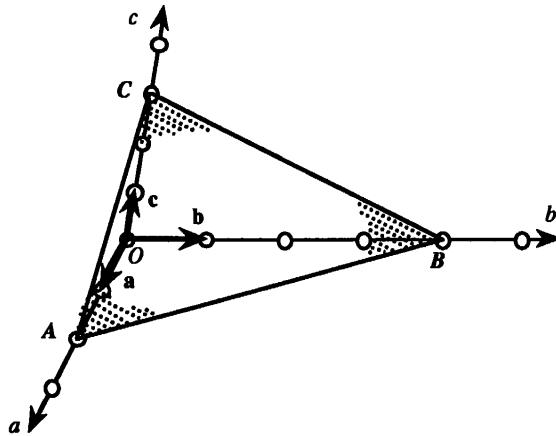


Figure 1.9 A (634) plane in a crystal lattice.

The orientation of crystal planes within the lattice is specified by a set of three integers referred to as the *Miller indices* of the planes. The Miller indices of crystal planes such as those illustrated in Figure 1.9 can be obtained as follows:

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- (1) Take the origin at any lattice point in the crystal, and coördinate axes in the directions of the basis vectors of the unit cell.
  - (2) Locate the intercepts of a plane belonging to the desired system along each of the coördinate axes, and express them as integral multiples of the respective basis vectors along the crystal axes.
  - (3) Take the *reciprocals* of these numbers, and multiply through by the smallest factor that will convert them to a triad of integers  $(h, k, l)$ , having the same ratios. The quantity  $(hkl)$  is the required set of Miller indices for this system of planes.

Figure 1.9 illustrates a crystal plane whose intercepts are at twice the atomic spacing along the  $a$ -axis, at four times the atomic spacing along the  $b$ -axis, and at three times the atomic spacing along the  $c$ -axis. The Miller indices of the family of which this plane is a member are obtained by taking the reciprocals of these numbers, that is  $(1/2, 1/4, 1/3)$ , and converting this to the smallest possible integer triad by multiplying by 12, writing the result (without commas) as (634). In arriving at the Miller indices, the tacit assumption that no other plane of the system intersects any of the atoms along the line segments  $OA$ ,  $OB$ , and  $OC$  in Figure 1.9 is usually made.

In any structure, a given set of crystal planes has a geometry characterized by some specific arrangement and spacing of atoms, and adjacent planes of the set have a characteristic interplanar spacing which depends on the Miller indices. There may be certain sets of crystal planes, moreover, whose Miller indices differ by permutation of indices or signs, yet which have the same interplanar spacing, and whose atoms all have the same geometrical arrangement. Such sets of crystal planes are said to be *crystallographically equivalent*. The planes which define all the faces of the cubic cell in the s.c., b.c.c., and f.c.c. structures, for example, are all crystallographically equivalent. In *orthogonal* structures, the planes formed by assigning all possible permutations of minus signs to the Miller indices:

$$(hkl), (\bar{h}kl), (h\bar{k}l), (hk\bar{l}),$$

are all crystallographically equivalent. There are only 4 such permutations, because when the signs of all three indices are reversed, the resulting plane is not merely equivalent but is parallel—which is viewed as crystallographically *identical*—to the original one. Incidentally, you should note that negative Miller indices are conventionally written with the minus sign above the index, rather than before it. In *cubic* structures, all sets of planes represented by permutations of the three Miller indices among themselves (for example,  $(hkl)$ ,  $(hlk)$ ,  $(kh)$ , etc.) are also crystallographically equivalent.

When a plane is parallel to one or two of the crystal axes, the corresponding intercepts will be at infinity. Since the reciprocal of an infinite quantity is zero, the Miller indices derived from these intercepts will likewise be zero. The situation can be understood with reference to Figure 1.9. When the point  $C$  recedes to infinity along the  $c$ -direction, the plane rotates about line  $AB$  until it is parallel to the  $c$ -axis. The intercepts are then  $(2, 4, \infty)$ , and the Miller indices are now  $(210)$ . Subsequently, if point  $B$  recedes to infinity along  $OB$ , the plane rotates about a line normal to the  $ab$ -plane through  $A$  until it is normal to the  $a$ -axis. The intercepts are now  $(2, \infty, \infty)$ , and the Miller indices become  $(100)$ . As noted above, the Miller indices of a particular set of planes are enclosed within ordinary parentheses. A complete set of crys-

allographically equivalent planes of which  $(hkl)$  is a member is written using curly brackets, thus:  $\{hkl\}$ .

It is possible also to assign numerical indices to directions within the crystal lattice. The indices of a *direction* in a crystal are expressed as a set of integers having the same ratios as the components of a vector from one lattice point to another, expressed as multiples of the respective basis vectors. Thus, the indices of a vector of the form  $ha + kb + lc$  is written—using square brackets—as  $[hkl]$ . Directions having different indices may be crystallographically equivalent in the same sense as crystal planes. Normals to crystallographically equivalent planes are crystallographically equivalent directions. However, except in cubic crystals, the  $[hkl]$  direction is not necessarily normal to the  $(hkl)$  plane. The complete set of crystallographically equivalent directions that includes  $[hkl]$  is written, using angle brackets, as  $\langle hkl \rangle$ . The orthogonality of the direction  $[hkl]$  to the plane  $(hkl)$  in cubic lattices provides a strong motivation for using cubic rather than primitive cells whenever possible for the b.c.c. and f.c.c. structures.

From Figure 1.9, it might appear that the spacing between adjacent planes of the  $(hkl)$  system is the distance between the origin and the plane which is shown. This is not true, however, because the origin can be taken at any lattice point of the crystal, which means, in effect, that *a plane of the  $(hkl)$  system must pass through every lattice point*, as illustrated in Figure 1.10. For this reason, the spacing between adjacent planes is ordinarily smaller than the interatomic spacing.

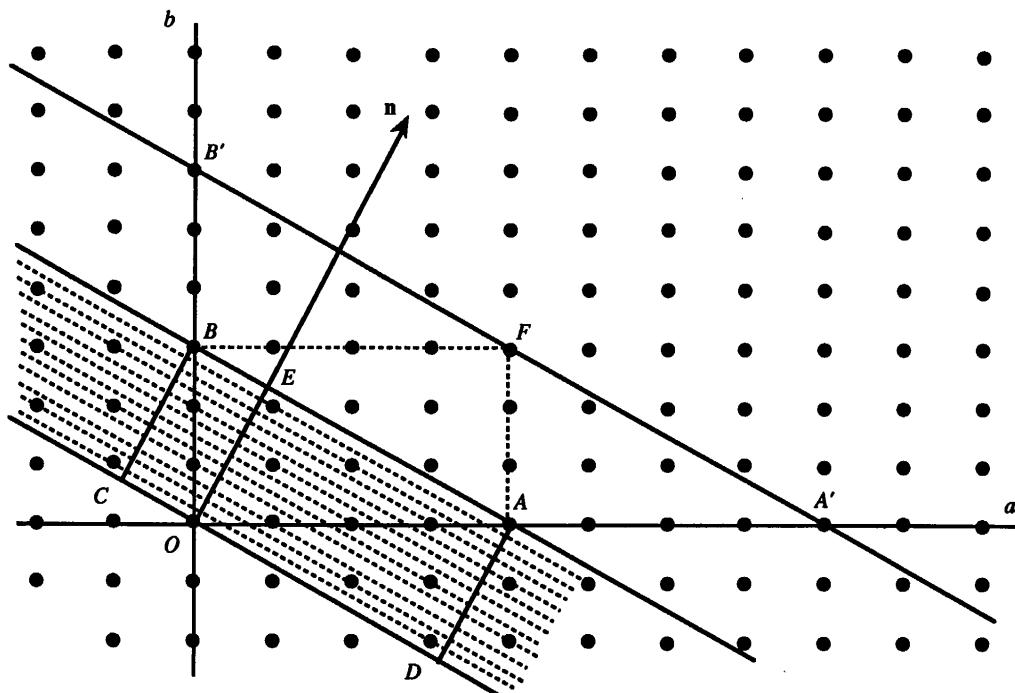


Figure 1.10. A family of (340) planes in an orthogonal crystal. The slanted lines represent the intersections of the planes, which are normal to the page, with the  $ab$ -plane of the unit cell.

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In the figure, a set of (340) planes is shown. These planes are parallel to the  $c$ -axis of the crystal, and therefore normal to the page. There are in this example only two nonzero Miller indices. This simplifies the subsequent analysis, but still permits a more general result to be inferred. Let  $m$  and  $n$  be the number of interatomic spacings between  $OA$  and  $OB$ , respectively; in the case illustrated,  $m = 4$  and  $n = 3$ . The Miller indices are obtained by taking the reciprocals of these numbers and multiplying by the smallest factor needed to obtain a pair of integers. If  $m$  and  $n$  have no common factor, this number will simply be the factor  $mn$ . We shall (again for simplicity) assume this to be the case, initially at least. The Miller indices will then be given by

$$h = \frac{mn}{m} = n \quad \text{and} \quad k = \frac{mn}{n} = m . \quad (1.5 - 1)$$

Now consider the area  $OBFA$ . Our usual scheme of assigning atoms to cells informs us that there are  $mn$  atoms in this region. Since region  $ABCD$  clearly has the same area as  $OBFA$ , it must also contain  $mn$  atoms. But since exactly one plane of the system intersects each atom of the crystal, there must be  $mn$  planes within  $ABCD$ . If you count the number of planes along  $OE$  in the figure, you will see that this is correct. Since all these planes intersect both of the crystal axes illustrated above, and since there are  $m$  atom spacings along  $OA$ , and  $n$  along  $OB$ , the distances  $d_a$  and  $d_b$  between intercepts of adjacent planes along the respective crystal axes are

$$d_a = \frac{ma}{mn} = \frac{a}{h} \quad \text{and} \quad d_b = \frac{nb}{mn} = \frac{b}{k} . \quad (1.5 - 2)$$

There is still the question of what happens when the multiplying factor used to arrive at the Miller indices is not precisely  $mn$ . This occurs whenever  $m$  and  $n$  have a common factor. In the example shown in Figure 1.10, such a situation would have arisen had the plane  $A'B'$  rather than  $AB$  been chosen initially to define the Miller indices. If we now let  $m = \alpha m'$  and  $n = \alpha n'$ , where  $\alpha$  is an integral common factor, (1.5 - 1) yields  $h = \alpha m'$  and  $k = \alpha n'$ ; substituting these values into (1.5 - 2), however, leaves this expression unchanged. It may also be noted that though an orthogonal system has been used for simplicity in the figure, there is nothing in the equations written above that depends on the choice of such a system. The results are valid in any system.

It is possible to carry out the calculation outlined above for a family of planes having three nonzero Miller indices, and which are therefore not parallel to any of the crystal axes. A full description of this calculation, and a rigorous treatment of cases where two, or all three, of the indices have a factor in common is tedious, time-consuming, and in the end leads to no unexpected results. The case where the three indices have no common factor is assigned as a problem for the reader, who should in any event have no trouble in accepting the result that in general, the spacing between the intercepts of adjacent  $(hkl)$  crystal planes along the three crystal axes is given by

$$d_a = \frac{a}{h} , \quad d_b = \frac{b}{k} , \quad \text{and} \quad d_c = \frac{c}{l} . \quad (1.5 - 3)$$

The actual interplanar spacing,  $d_{hkl}$  can now be obtained by calculating the scalar product of the vector  $\mathbf{d}_a = \mathbf{a}/h$  with a unit vector  $\mathbf{n}$  normal to the planes. In fact, we can write

$$d_{hkl} = \frac{\mathbf{n} \cdot \mathbf{a}}{h} = \frac{\mathbf{n} \cdot \mathbf{b}}{k} = \frac{\mathbf{n} \cdot \mathbf{c}}{l} . \quad (1.5 - 4)$$

In *orthogonal* systems having one atom per cell, this spacing can be stated more explicitly by noting that the  $(hkl)$  plane closest to the origin has intercepts  $a/h$ ,  $b/k$ ,  $c/l$ , along the three axes. If the axes are orthogonal, the equation of this plane in cartesian coördinates can be written as

$$f(x, y, z) = \frac{x}{(a/h)} + \frac{y}{(b/k)} + \frac{z}{(c/l)} = 1 . \quad (1.5 - 5)$$

This is the equation of a surface--a plane in this case--having the form  $f(x, y, z) = \text{constant}$ . A vector normal to such a surface can be found by calculating the gradient of the function  $f(x, y, z)$ , and if this gradient is divided by its own magnitude, the result will be the unit normal vector  $\mathbf{n}$ . We can thus write,

$$\nabla f = i_x \frac{\partial f}{\partial x} + i_y \frac{\partial f}{\partial y} + i_z \frac{\partial f}{\partial z} = i_x \frac{h}{a} + i_y \frac{k}{b} + i_z \frac{l}{c} , \quad (1.5 - 6)$$

where  $i_x$ ,  $i_y$ , and  $i_z$  are *unit* vectors along the cartesian axes, which now coincide with the crystal axes. Thus,

$$\mathbf{n} = \frac{\nabla f}{|\nabla f|} = \frac{i_x(h/a) + i_y(k/b) + i_z(l/c)}{\sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}} . \quad (1.5 - 7)$$

The distance  $d_{hkl}$  between adjacent planes can now be obtained from (1.5-4) as the scalar product of this vector and the vector  $\mathbf{a}/h$ , which in the cartesian system has only an  $x$ -component, and can be written as  $i_x a/h$ . The result is

$$d_{hkl} = \frac{1}{\sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}} . \quad (1.5 - 8)$$

## 1.6 THE RECIPROCAL LATTICE

When a beam of X-rays--or particles such as electrons--is directed at a crystal, it is observed that a complex system of outgoing diffracted beams in various directions is produced by Bragg reflection from the numerous sets of crystal planes in the lattice. If these diffracted beams gave direct information about the crystal lattice itself, there would be no need for this section, but instead the information they convey is most directly related to another lattice referred to as the *reciprocal lattice* of the

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crystal. The real space lattice of the crystal must then be inferred from the reciprocal lattice by a set of transformation equations which define the geometrical relationship between the two lattices. There are many other instances in which the reciprocal lattice turns out to be a useful construct, so it will be advantageous to introduce it at this point even though its full utility may not be immediately apparent.

In defining the unit cell of the reciprocal lattice it is necessary to start with the *primitive* unit cell of the direct space lattice of the crystal. If  $\mathbf{a}$ ,  $\mathbf{b}$ , and  $\mathbf{c}$  are primitive basis vectors of the direct lattice, a set of primitive basis vectors  $\mathbf{a}^*$ ,  $\mathbf{b}^*$ , and  $\mathbf{c}^*$  of the reciprocal lattice will be generated by the following relations:

$$\mathbf{a}^* \cdot \mathbf{a} = \mathbf{b}^* \cdot \mathbf{b} = \mathbf{c}^* \cdot \mathbf{c} = 1 \quad (1.6 - 1)$$

$$\text{and } \mathbf{a}^* \cdot \mathbf{b} = \mathbf{a}^* \cdot \mathbf{c} = \mathbf{b}^* \cdot \mathbf{c} = \mathbf{b}^* \cdot \mathbf{a} = \mathbf{c}^* \cdot \mathbf{a} = \mathbf{c}^* \cdot \mathbf{b} = 0 . \quad (1.6 - 2)$$

From (1.6-2), since the scalar product of  $\mathbf{a}^*$  with both  $\mathbf{b}$  and  $\mathbf{c}$  is zero,  $\mathbf{a}^*$  is perpendicular to both  $\mathbf{b}$  and  $\mathbf{c}$ , and thus to the plane determined by them. It is therefore in the direction of the vector  $\mathbf{a} \times \mathbf{b}$ , and can therefore be written as a multiple of that vector,

$$\mathbf{a}^* = A(\mathbf{b} \times \mathbf{c}) , \quad (1.6 - 3)$$

where  $A$  is a scalar constant. This constant can be evaluated using (1.6-1), whereby

$$\mathbf{a}^* \cdot \mathbf{a} = A(\mathbf{b} \times \mathbf{c}) \cdot \mathbf{a} = 1 . \quad (1.6 - 4)$$

Solving for  $A$  and substituting its value into (1.6-3), we find

$$\mathbf{a}^* = \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}}$$

In the same way, it can be shown that

$$\mathbf{b}^* = \frac{\mathbf{c} \times \mathbf{a}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}} \quad \text{and} \quad \mathbf{c}^* = \frac{\mathbf{a} \times \mathbf{b}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}} .$$

Using the same methods, one can also obtain inverse transformations, of the form

$$\mathbf{a} = \frac{\mathbf{b}^* \times \mathbf{c}^*}{\mathbf{a}^* \cdot \mathbf{b}^* \times \mathbf{c}^*} . \quad (1.6 - 6)$$

The remaining inverse transformations can obviously be written merely by interchanging starred and unstarred symbols in (1.6-5).

For a simple cubic lattice of interatomic spacing  $a$ ,  $\mathbf{a} = ai_x$ ,  $\mathbf{b} = ai_y$ ,  $\mathbf{c} = ai_z$ . If these vectors are substituted into equations (1.6-5), the result is

$$\mathbf{a}^* = (1/a)\mathbf{i}_x , \quad \mathbf{b}^* = (1/a)\mathbf{i}_y , \quad \text{and} \quad \mathbf{c}^* = (1/a)\mathbf{i}_z . \quad (1.6 - 7)$$

This is another simple cubic structure, of lattice spacing  $1/a$ . From this, it is evident that the s.c. lattice is self-reciprocal. Note, however, that the dimensions of the reciprocal lattice are reciprocal distances. The units are those of the propagation constants of waves, suggesting that vectors in the reciprocal lattice might naturally be associated with the propagation vectors of diffracted radiation.

Consider now the case of a b.c.c. direct lattice, such as the one shown in Figure 1.5(a). For the primitive cell illustrated there, assuming the  $x$ -direction toward the reader, the  $y$ -direction to the right, and the  $z$ -direction upward, the primitive basis vectors are

$$\mathbf{a} = \frac{L}{2}(\mathbf{i}_x - \mathbf{i}_y + \mathbf{i}_z), \quad \mathbf{b} = \frac{L}{2}(-\mathbf{i}_x - \mathbf{i}_y + \mathbf{i}_z), \quad \mathbf{c} = \frac{L}{2}(\mathbf{i}_x + \mathbf{i}_y + \mathbf{i}_z), \quad (1.6 - 8)$$

where  $L$  is the edge of the cubic cell. Substituting these into (1.6 - 5), performing the indicated vector algebra, and simplifying, one may obtain the reciprocal lattice vectors

$$\mathbf{a}^* = \frac{1}{L}(\mathbf{i}_x - \mathbf{i}_y), \quad \mathbf{b}^* = \frac{1}{L}(-\mathbf{i}_x + \mathbf{i}_z), \quad \mathbf{c}^* = \frac{1}{L}(\mathbf{i}_y + \mathbf{i}_z). \quad (1.6 - 9)$$

These are easily identified as primitive basis vectors of an f.c.c. structure, like the one illustrated in Figure 1.5(b). Though different from the basis vectors in that diagram, they are identical to the equivalent set of basis vectors that would stem from choosing an origin at the face-center atom at the bottom of the cell. In a similar way, one can show that the reciprocal lattice associated with the f.c.c. structure is a b.c.c. lattice. Other reciprocal structures can be exhibited in the same way.

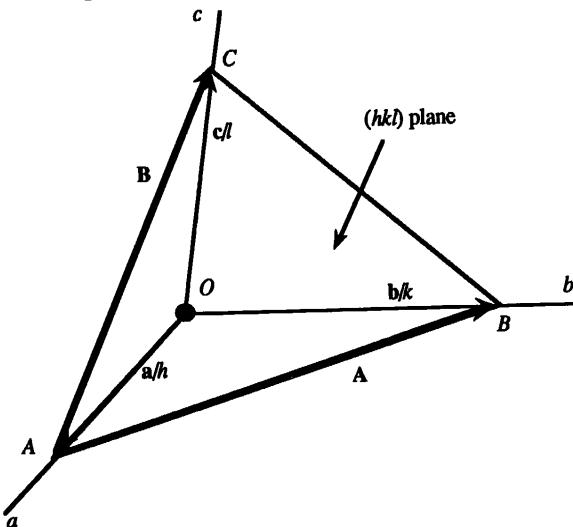


Figure 1.11 Direct lattice vector geometry for the derivation of Equations (1.6 - 11) and (1.6 - 13).

The geometries of the direct and reciprocal lattices are related by the fact that a vector  $\mathbf{r}^* = h'\mathbf{a}^* + k'\mathbf{b}^* + l'\mathbf{c}^*$  from the origin to any lattice point of the reciprocal lattice is normal to the  $(hkl)$  plane of the *direct* lattice, where  $(hkl)$  and  $(h'k'l')$  are identical except (possibly) for the presence of a common factor  $N$ , so that

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$$\frac{h'}{h} = \frac{k'}{k} = \frac{l'}{l} = N . \quad (1.6 - 10)$$

This can be proved with reference to Figure 1.11, which illustrates the  $(hkl)$  plane adjacent to the origin, which is chosen at a lattice point. Clearly, both vectors  $\mathbf{A}$  and  $\mathbf{B}$  lie in the  $(hkl)$  plane. Then,

$$\mathbf{r}^* \cdot \mathbf{B} = \mathbf{r}^* \cdot [(\mathbf{c}/l) - (\mathbf{a}/h)] = (h'\mathbf{a}^* + k'\mathbf{b}^* + l'\mathbf{c}^*) \cdot [(\mathbf{c}/l) - (\mathbf{a}/h)] = \frac{l'}{l} - \frac{h'}{h} = 0,$$

and

$$\mathbf{r}^* \cdot \mathbf{A} = \mathbf{r}^* \cdot [(\mathbf{b}/k) - (\mathbf{a}/h)] = (h'\mathbf{a}^* + k'\mathbf{b}^* + l'\mathbf{c}^*) \cdot [(\mathbf{b}/k) - (\mathbf{a}/h)] = \frac{k'}{k} - \frac{h'}{h} = 0.$$

The vector  $\mathbf{r}^*$  is clearly perpendicular to two independent vectors,  $\mathbf{A}$  and  $\mathbf{B}$ , which lie in the  $(hkl)$  plane. It must therefore be perpendicular to the plane itself. Moreover, if  $\mathbf{n}$  is a unit vector perpendicular to the plane, we may write  $\mathbf{n} = \mathbf{r}^*/r^*$ , and the distance between adjacent  $(hkl)$  planes can be expressed, using (1.6-1), as

$$d_{hkl} = \frac{\mathbf{n} \cdot \mathbf{a}}{h} = \frac{\mathbf{a} \cdot \mathbf{r}^*}{hr^*} = \frac{\mathbf{a} \cdot (h'\mathbf{a}^* + k'\mathbf{b}^* + l'\mathbf{c}^*)}{hr^*} = \frac{N}{r^*} . \quad (1.6 - 12)$$

The magnitude of the vector  $\mathbf{r}^*$  is now seen to be directly related to the reciprocal of the interplanar spacing in the direct lattice by

$$r^* = \frac{N}{d_{hkl}} , \quad (1.6 - 13)$$

where  $N$  is the integer defined by (1.6-10).

## 1.7 INTERATOMIC FORCES IN CRYSTALS

We are now at the end of our survey of crystallography, and can profitably look more closely at the interatomic forces that hold crystals together and ensure the stability of condensed matter. These forces have already been mentioned, but only in a very cursory way. This discussion will be more detailed, though by no means exhaustive. Indeed, we shall return to this subject again and again to develop a deeper and more quantitative understanding of what is still an important and active research area in condensed-matter physics.

The first fundamental interparticle force we learn about in elementary physics is gravity, which is usually presented as a macroscopic force between relatively massive bodies, but is naturally present on the atomic level also. However, its effects on this level are generally negligible, for it is many orders of magnitude weaker than the electromagnetic forces which are of primary importance in holding crystals together. The simplest of these electromagnetic interactions is the electrostatic force between charged particles. The electrostatic force, as defined by Coulomb's law, is like gravity, an inverse square interaction, but may be either attractive or repulsive, depending on the signs of the charges. On the atomic level, however, the way in

which this simple classical force acts is governed by the requirements of quantum theory and chemical valency, which is in itself a quantum effect. These requirements modify to a significant extent electrostatic interactions in the atomic realm.

Chemical valency is an aspect of atomic structure arising directly from the periodic table of the elements. The periodic table and the concept of valence were in everyday use long before quantum theory was developed, but the basic justification of these ideas rests upon fundamental principles of atomic physics which in turn follow directly from quantum mechanics. At this point we must rely heavily upon classical notions of chemical valence, but as we progress the connections with quantum mechanics will become increasingly evident.

Ionic crystals typically unite elements from column I and column VII of the periodic table. The most common substance of this type is sodium chloride, NaCl. In sodium atoms the outer valence electron is loosely bound, and the atom is easily ionized, while chlorine atoms have an extremely strong affinity for electrons that will complete their valence octet and transform them into negative ions. Such substances are ionized not only in aqueous solution, but also in their crystalline form. In the NaCl crystal illustrated in Figure 1.8, then, there are monovalent positive ions on Na sites and monovalent negative ions on Cl sites. Acting on any given ion, there are repulsive forces from other ions of like sign as well as attractive ones from oppositely charged ions. Since all the nearest neighbors to any given ion are of opposite sign, however, the resultant interaction is attractive, and the crystal is in fact bound together by these forces. As the electron distributions of neighboring atoms begin to overlap--that is as the atoms begin to touch one another--repulsive forces begin to develop and to oppose the effect of simple electrostatic attraction, until a final equilibrium is reached in which the ions are typically a few Ångströms apart. In NaCl, the equilibrium interatomic distance is about 2.8Å, i.e.,  $2.8 \times 10^{-10}$ m. Ionic substances are usually transparent to visible light; moreover, they exhibit a strong peak in optical reflectivity at a well-defined frequency in the far infrared. They are usually poor electrical conductors at room temperature. They have relatively high melting points and low vapor pressures, and they often crystallize in the compact NaCl and CsCl structures.

In Column IV, in the center of the periodic table, we find the tetravalent elements carbon, silicon, germanium, and tin. These elements have little or no tendency to form ions, either in aqueous solution or in the crystalline state. Instead, they tend to share their valence electrons with one another, forming covalent electron-pair bonds between neighboring atoms. We have already mentioned these properties in our previous study of the diamond lattice, in which these elements tend to crystallize. Unlike ionic substances, there is no transfer of charge from one atom to another in covalent crystals; since electrons are shared equally, the atoms are electrically neutral. Quantum theory shows that electron-pair covalent bonds can be very strong and stable links between covalent atoms. Crystals of diamond, silicon, and germanium are therefore very hard and strong, though somewhat brittle. They are relatively stable substances with high melting points. They are typically transparent to infrared radiation, though opaque to ultraviolet and (with the obvious exception of diamond) visible light. The infrared reflectivity peak mentioned in connection with ionic crystals is no longer observed. Germanium, silicon, and diamond, as a direct result of their covalent bonding, are semiconductors. In the pure form they exhibit a limited electrical conductivity that increases with

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temperature, particularly at high temperatures, and is moreover strongly influenced by the addition of minute quantities of certain types of impurity atoms. The nearest-neighbor interatomic distance--the distance AB in Figure 1.7--is, for germanium 2.45Å, for silicon 2.35Å, and for diamond 1.54Å.

It thus appears that covalency is a way of life in the center of the periodic table, while ionic behavior is the norm at the edges. These two diametrically opposed scenarios, however, are not mutually exclusive. While I-VII compounds are highly ionic, and group IV elements are exclusively covalent, there is a *mixture* of ionic and covalent bonding in the intermediate II-VI and III-V compounds, the former being primarily ionic though somewhat covalent, the latter mostly covalent in character, though slightly ionic. In II-VI compounds, such as ZnS, electron transfer from zinc to sulfur atoms is not quite complete; though the valence electrons reside mostly on sulfur sites, there is a slight tendency for them to be shared with zinc atoms, and to be found on zinc sites. In III-V materials like GaAs, the substance is mostly covalent in character, with a strong network of electron-pair bonds in place to bind the atoms together. These compounds are semiconductors which crystallize in the zincblende structure, whose form is almost identical to that of the diamond lattice. The sharing of electrons between the two atomic species is not quite symmetrical, however, for there is a small net positive charge associated with gallium sites and a corresponding negative charge on arsenic atoms.

Metallic substances present a physical picture entirely different from ionic and covalent materials. In ionic and covalent crystals, electrons are mostly immobile, being either tightly bound to the ions or tied up in a network of covalent pair bonds. In metallic crystals, however, the valence electrons are no longer associated with any particular atomic site, but are free to move at large within the crystal. In effect, they form a free-particle gas for which the crystal serves as a container. The electronic properties of the crystal are then primarily those of the gas of mobile electrons within it. The crystal is held together by a net electrostatic attraction between the positively charged immobile lattice ions and the gas of negatively charged electrons; the net attractive interaction arises in somewhat the same way as in ionic materials, except that the negative charges are no longer regularly spaced, but are randomly distributed. Since the valence electrons are free to move in the direction of an applied electric field, metallic substances conduct electricity freely. They are also good conductors of heat, and display high optical surface reflectivity and strong optical absorption within the material; these properties are also directly related to the presence of the the free electron gas.

Still another type of crystal binding is found in crystals of solid organic substances, such as naphthalene or benzoic acid. In these molecular crystals, the lattice sites are occupied by complete molecules which are electrically neutral. Neutral molecules, however, may posess intrinsic electric dipole moments if their internal charge distribution is asymmetric. Moreover, even molecules which have no intrinsic or permanent electric dipole moment can exhibit fluctuating *instantaneous* dipole moments arising from momentary fluctuations of the electronic charge distribution within the molecule. These instantaneous dipole configurations can induce oppositely directed dipole moments in neighboring molecules, much as a point charge or dipole can induce an image charge or image dipole of opposite sign in a nearby conductor. The force between an inducing dipole and the induced dipole is attractive, and can therefore act to bind the crystal together, in spite of the fact

that the time-average dipole moment of the molecules may be zero. Binding forces that arise in this manner are referred to as *Van der Waals forces*. Since these forces are between dipoles rather than charged particles, they are much weaker than the binding forces in ionic crystals. Molecular binding is therefore comparatively weak, resulting in crystals that have relatively low melting points. Inert gases like neon and argon in the solid state also form crystals bound by Van der Waals forces.

When the energy difference between two different possible structures is relatively small, and when a significant potential energy barrier must be overcome to transform one into the other, it may be possible for both forms to exist as stable configurations at the same temperature and pressure. This phenomenon is referred to as *allotropy*, and the two different configurations are called *allotropes*, or *allotropic forms*. In such instances, of course, one form will be thermodynamically stable, while the other is metastable--that is, theoretically unstable with respect to the other, but inhibited from making a transformation by the potential energy barrier which must be surmounted. Two of the most familiar examples are carbon and tin. In the case of carbon, the allotropic forms are graphite and diamond, the latter being metastable under normal conditions. In regard to tin, the two allotropes are referred to as gray tin and white tin--or, sometimes,  $\alpha$ - and  $\beta$ -tin. At room temperatures, the familiar "white" metallic tin, which has a tetragonal lattice, is the thermodynamically stable form, but below 286.4K the gray form, which crystallizes in the diamond structure, becomes the stable allotrope. Gray tin is another group IV covalent semiconductor, with properties similar to silicon and germanium. In this regard it is as strikingly different from the metallic white form as diamond is from graphite.

There are also substances whose long-range order lacks the property of translational invariance and is instead based on a polyhedral ordering scheme. Such substances, referred to as *quasicrystals*, sometimes display fivefold rotational symmetry, which is geometrically impossible in translationally invariant space lattices.

In this discussion, and in the preceding material, it is apparent that crystal lattices--and atoms as well--are built on the scale of Ångström units. The table of crystal properties and cell sizes below should make this fact even more evident. It is also important to recognize that a connection between the macroscopic properties of crystalline substances and the microworld of the lattice is provided by Avogadro's number,  $N_A = 6.022 \times 10^{23}$  mole<sup>-1</sup>, which gives the number of molecules or atoms per gram-mole. This fact is useful in working many of the exercises that follow.

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## PHYSICAL DATA FOR SIMPLE CRYSTALLINE SOLIDS

| Substance                 | Lattice    | Cell edge, Å | Density, g/cm³ | M. P., K | B.P., K |
|---------------------------|------------|--------------|----------------|----------|---------|
| <b>IONIC</b>              |            |              |                |          |         |
| NaCl                      | NaCl       | 5.64         | 2.17           | 1074     | 1686    |
| KCl                       | NaCl       | 6.29         | 1.98           | 1049     | subl.   |
| NaBr                      | NaCl       | 5.95         | 3.20           | 1028     | 1663    |
| KBr                       | NaCl       | 6.58         | 2.75           | 1003     | 1708    |
| NaI                       | NaCl       | 6.46         | 3.67           | 924      | 1577    |
| KI                        | NaCl       | 7.05         | 3.13           | 959      | 1603    |
| CsCl                      | CsCl       | 4.11         | 3.99           | 919      | 1563    |
| AgCl                      | NaCl       | 5.55         | 5.56           | 728      | 1823    |
| AgBr                      | NaCl       | 5.77         | 6.47           | 705      | dec.    |
| <b>COVALENT and III-V</b> |            |              |                |          |         |
| C(diam)                   | diamond    | 3.56         | 3.51           | 4300     | 5500    |
| Si                        | d          | 5.42         | 2.328          | 1685     | 2628    |
| Ge                        | d          | 5.62         | 5.323          | 1231     | 3103    |
| $\alpha$ -Sn              | d          | 6.46         | 5.76           | 503      | 2540    |
| GaAs                      | zincblende | 5.64         | 5.32           | 1510     | dec.    |
| GaP                       | z          | 5.45         | 4.13           | 1750     | dec.    |
| InSb                      | z          | 6.48         | 5.78           | 798      | dec.    |
| InP                       | z          | 5.87         | 4.79           | 1330     | dec.    |
| <b>METALLIC</b>           |            |              |                |          |         |
| Na                        | bcc        | 4.29         | 0.97           | 371      | 1156    |
| K                         | bcc        | 5.20         | 0.86           | 337      | 1047    |
| Cu                        | fcc        | 3.62         | 8.92           | 1356     | 2840    |
| Ag                        | fcc        | 4.09         | 10.5           | 1235     | 2485    |
| Au                        | fcc        | 4.08         | 19.3           | 1337     | 3080    |
| Fe                        | bcc        | 2.87         | 7.86           | 1808     | 3023    |
| Al                        | fcc        | 4.04         | 2.70           | 933      | 2740    |
| Pb                        | fcc        | 4.95         | 11.34          | 601      | 2013    |
| $\beta$ -Sn               | tetr       | 5.83, 3.18   | 7.28           | 508      | 2540    |
| <b>VAN DER WAALS</b>      |            |              |                |          |         |
| Ar                        | fcc        | 5.43 (4K)    | 1.66 (4K)      | 84.0     | 87.5    |
| Ne                        | fcc        | 4.52 (4K)    | 1.45 (4K)      | 24.5     | 27.2    |
| Kr                        | fcc        | 5.59 (20K)   | 3.19 (20K)     | 116.6    | 120.9   |
| Xe                        | fcc        | 6.20 (88K)   | 3.66 (88K)     | 161.3    | 166.1   |

## PROBLEMS

1. The density of copper is  $8.92 \text{ g/cm}^3$ , and its molar mass is  $63.54 \text{ g/mole}$ . Using these data, and elementary principles of physics and chemistry, calculate the nearest-neighbor interatomic spacing between atoms in the f.c.c lattice of copper. Compare your answer with the value calculated from the data in the above table.
2. The molar mass of argon is  $39.95 \text{ g/mole}$ . Assuming that argon is an ideal gas at normal temperature and atmospheric pressure, calculate the density of argon at atmospheric pressure and temperature 300K. How many atoms per unit volume are there under these conditions, assuming a monatomic gas? What is the average distance between atoms under these conditions? Compare these answers with those obtained for crystalline copper in Problem 1.
3. From the data in the above table, calculate the interatomic spacing (distance AB in Figure 1.7) in crystalline silicon. How many atoms are there per unit volume ( $\text{cm}^{-3}$ )?
4. A cubic crystal's cubic cell edge is  $3.6\text{\AA}$ . Write an expression for a lattice vector from an atom at the origin to one 2 cells away along the **a**-axis, 4 cells away along the **b**-axis, and 6 cells distant along the **c**-direction. What is the length of this vector, and what are the angles it makes with the three crystal axes?
5. Work problem 4 for a monoclinic lattice where the cell edges are  $a = 2\text{\AA}$ ,  $b = 3.6\text{\AA}$ ,  $c = 2.4\text{\AA}$ , and where the angle between the **a**- and **b**-axes is  $60^\circ$ .
6. When substances which normally crystallize in the b.c.c. or diamond structures are subjected to very high hydrostatic pressure, a phase transition to an f.c.c. structure sometimes occurs. Can you suggest a qualitative physical explanation for this fact?
7. Using the three-dimensional lattices shown in Figure 1.3 as a starting point, show that in two dimensions, the number of possible Bravais lattices is reduced to 5. Show explicitly the geometry of these five lattices.
8. Crystal lattices having five-fold rotational symmetry—that is, which are translationally invariant under rotations of  $360/5$  or  $72$  degrees about some axis—do not occur in nature. Can you give a geometrical explanation for this observation?
9. Show that a face-centered tetragonal arrangement of atoms is the same as a body-centered tetragonal lattice like the one shown in Figure 1.3, in which the base of the unit cell is  $\sqrt{2}/2$  times that of the face-centered cell. Why are the face-centered and body-centered *cubic* lattices different?
10. Considering the atoms to be hard spheres of equal radii in contact along the line between nearest neighbors, find the fraction of the volume of the unit cell occupied by the atoms for the s.c., b.c.c., f.c.c., and diamond lattices.
11. With respect to an atom at the origin, a crystal plane intersects an atom two atomic spacings away along the **a**-axis, an atom four atomic spacings away along the **b**-axis, and an atom five atomic spacings away along the **c**-axis of the crystal. Find the Miller indices of this plane.
12. In a simple tetragonal crystal, the unit cell dimensions are  $a = b = 1.80\text{\AA}$ ,  $c = 2.40\text{\AA}$ . Find the spacing between adjacent (111) planes and adjacent (523) planes in this crystal.
13. For the crystal structure described in the preceding problem, find the distance between adjacent atoms along the [111] direction and along the [523] direction.
14. In a face-centered cubic crystal, the spacing between adjacent (221) planes is  $1.20\text{\AA}$ . The molar mass of the atoms is  $60\text{g/mole}$ . What is the density of this substance in the crystalline state?

15. Prove that in a cubic crystal the  $[hkl]$  direction is orthogonal to the  $(hkl)$  plane.
16. In an orthogonal lattice, derive an expression for the angle between the  $[hkl]$  direction and the normal to the  $(hkl)$  plane.
17. Derive the intercept spacings given in Equation (1.5 - 3) for a three-dimensional orthogonal lattice. You may assume that there are no integer factors common to any pair of atom spacings or Miller indices.
18. Draw simple sketches illustrating the  $\{100\}$ ,  $\{110\}$ , and  $\{111\}$  planes in a cubic unit cell.
19. How many equivalent  $\{111\}$  planes are there in a cubic lattice? How many equivalent  $\{122\}$  planes? How many equivalent  $\{123\}$  planes?
20. What would the answers to the preceding problem be for an orthorhombic lattice?
21. Obtain an expression for the number of atoms per unit area in an  $(hkl)$  plane, in terms of the lattice parameters and interplanar spacing.
22. Find the reciprocal lattice for a two-dimensional simple square lattice of interatomic spacing  $a$ . Observe that you cannot define vector cross products in two dimensions.
23. Find the reciprocal lattice for a two-dimensional hexagonal array like the one in the base plane of the hexagonal structure illustrated in Figure 1.3.
24. Show that the face-centered cubic lattice has a body-centered cubic reciprocal lattice, using methods similar to those employed in Section 1.6.
25. Find the potential energy of binding between a chlorine atom and its nearest neighbor sodium atoms in the sodium chloride crystal. Express your answer in units of electron-volts (eV) per atom. Recall that  $1 \text{ eV} = 1.602 \times 10^{-19} \text{ joule}$ .
26. Show, using classical electrostatics, that the potential energy of an induced Van der Waals molecular dipole in an external inducing dipole field is proportional to  $r^{-6}$ , where  $r$  is the separation between dipoles. *Hint:* Recall that the potential energy of a point dipole in an external field is given by the scalar product of the dipole moment and the local external field.
27. Compare the electrostatic and Newtonian gravitational forces (a) between two electrons (b) between an electron and a proton (c) between an electron and a singly charged uranium 238 ion.

pation of heat by water-cooling, conduction, radiation, etc., how long would it take a 100-gm copper target to melt? (Melting point of copper =  $1083^{\circ}\text{C}$ , mean specific heat =  $6.65 \text{ cal/mole}/^{\circ}\text{C}$ , latent heat of fusion =  $3,220 \text{ cal/mole}$ .)

**1-18.** Assume that the sensitivity of x-ray film is proportional to the mass absorption coefficient of the silver bromide in the emulsion for the particular wavelength involved. What, then, is the ratio of film sensitivities to Cu  $K\alpha$  and Mo  $K\alpha$  radiation?

## CHAPTER 2

### THE 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.

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."

**2-2 Lattices.** 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 may be regarded as a sort of framework or skeleton on which the actual crystal is built up.

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 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

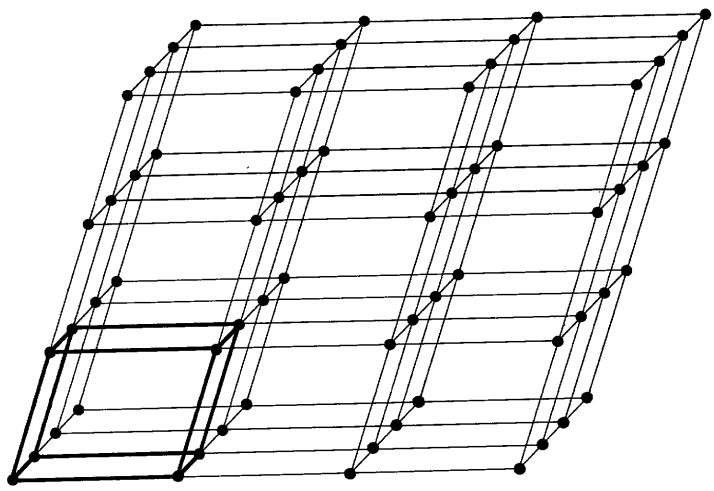


FIG. 2-1. A point lattice.

size and shape of the unit cell can in turn be described by the three vectors\*  $\mathbf{a}$ ,  $\mathbf{b}$ , and  $\mathbf{c}$  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 ( $\alpha$ ,  $\beta$ ,  $\gamma$ ). These lengths and angles are the  or  of the unit cell.

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 the 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.

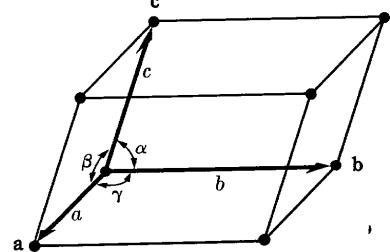


FIG. 2-2. A unit cell.

**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

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

TABLE 2-1  
CRYSTAL SYSTEMS AND BRAVAIS LATTICES

(The symbol  $\neq$  implies nonequality by reason of 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<br>$a = b = c$ , $\alpha = \beta = \gamma = 90^\circ$   | Simple<br>Body-centered<br>Face-centered                  | P<br>I<br>F      |
| Tetragonal    | Three axes at right angles, two equal<br>$a = b \neq c$ , $\alpha = \beta = \gamma = 90^\circ$   | Simple<br>Body-centered                                   | P<br>I           |
| Orthorhombic  | Three unequal axes at right angles<br>$a \neq b \neq c$ , $\alpha = \beta = \gamma = 90^\circ$   | Simple<br>Body-centered<br>Base-centered<br>Face-centered | P<br>I<br>C<br>F |
| Rhombohedral* | Three equal axes, equally inclined<br>$a = b = c$ , $\alpha = \beta = \gamma \neq 90^\circ$  | Simple  | R                |
| Hexagonal     | Two equal coplanar axes at $120^\circ$ , third axis at right angles<br>$a = b \neq c$ , $\alpha = \beta = 90^\circ$ , $\gamma = 120^\circ$ | Simple  | P                |
| Monoclinic    | Three unequal axes, one pair not at right angles<br>$a \neq b \neq c$ , $\alpha = \gamma = 90^\circ \neq \beta$                            | Simple<br>Base-centered                                   | P<br>C           |
| Triclinic     | Three unequal axes, unequally inclined and none at right angles<br>$a \neq b \neq c$ , $\alpha \neq \beta \neq \gamma \neq 90^\circ$       | Simple  | P                |

\* Also called trigonal.

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.

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*

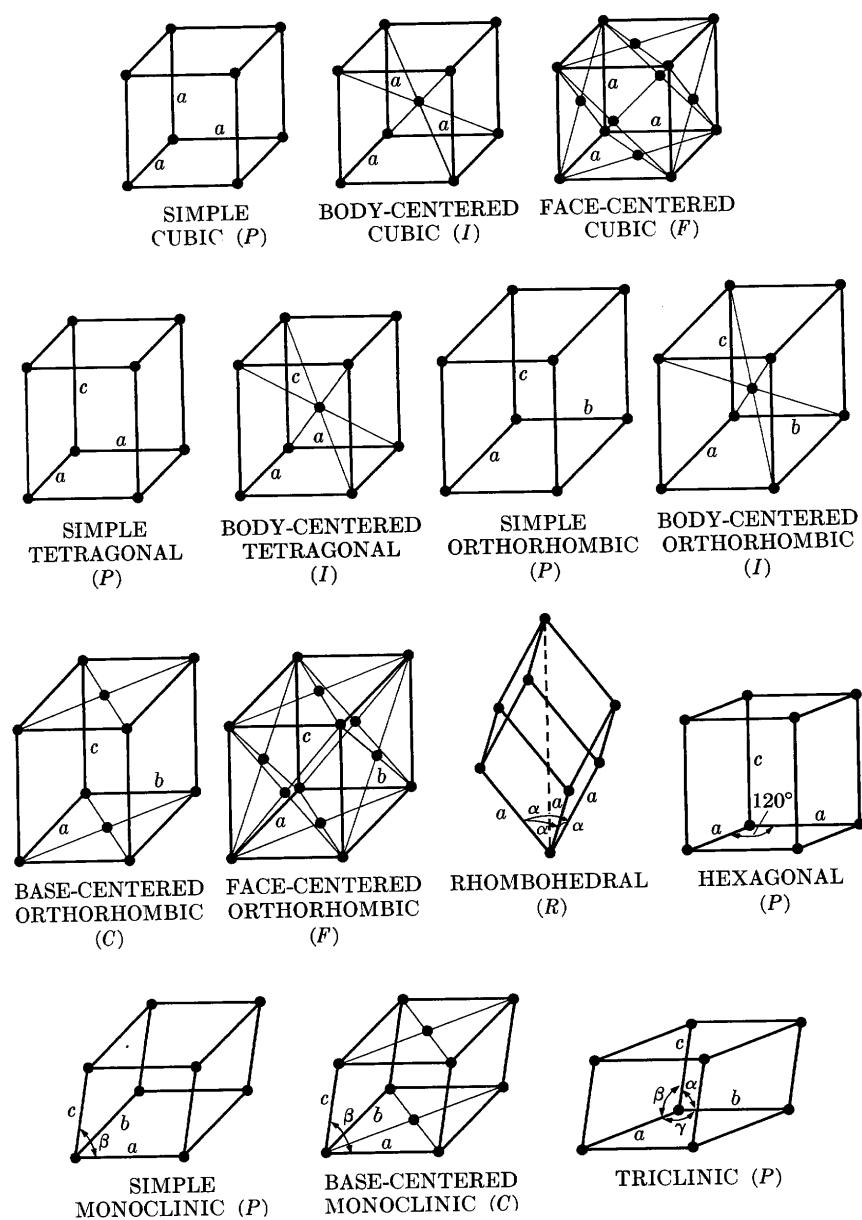


FIG. 2-3. The fourteen Bravais lattices.

*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

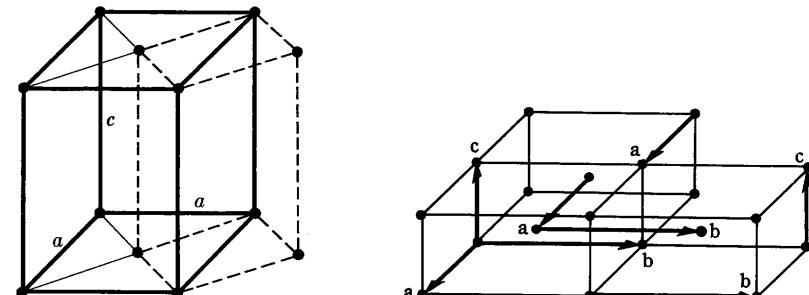
on a cubic unit cell having lattice points at each corner and in the center of each face.

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 *nonprimitive* 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 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.

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  $\mathbf{a}$ ,  $\mathbf{b}$ ,  $\mathbf{c}$  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  $\mathbf{a}$ ,  $\mathbf{b}$ ,  $\mathbf{c}$ , 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*, *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

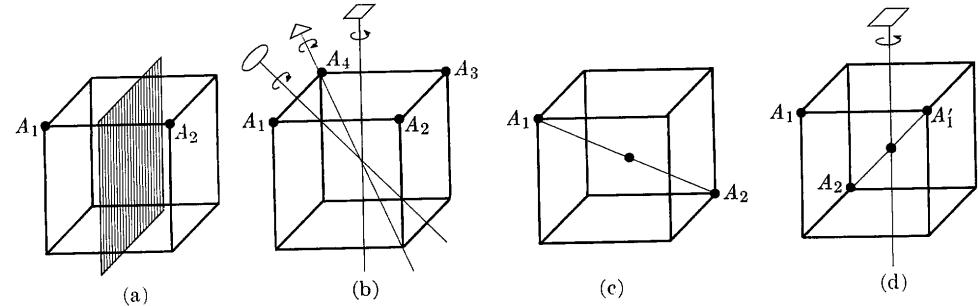


FIG. 2-6. Some symmetry elements of a cube. (a) Reflection plane.  $A_1$  becomes  $A_2$ . (b) Rotation axes. 4-fold axis:  $A_1$  becomes  $A_2$ ; 3-fold axis:  $A_1$  becomes  $A_3$ ; 2-fold axis:  $A_1$  becomes  $A_4$ . (c) Inversion center.  $A_1$  becomes  $A_2$ . (d) Rotation-inversion axis. 4-fold axis:  $A_1$  becomes  $A'_1$ ; inversion center:  $A'_1$  becomes  $A_2$ .

\* 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.

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 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. 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.

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

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   |

allowed; as mentioned before, however, this lattice is simple, not base-centered, tetragonal.

Crystals in the rhombohedral (trigonal) system can be referred to either a rhombohedral or a hexagonal lattice. Appendix 2 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  $\alpha$  is  $60^\circ$ , 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.

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

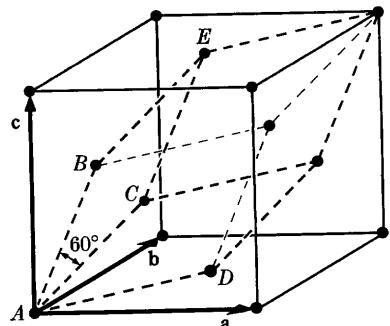


FIG. 2-7. Face-centered cubic point lattice referred to cubic and rhombohedral cells.

to point  $D$ , being separated from it by the vector  $\mathbf{c}$ . The coordinates 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  $\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$  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  $0\ 0\ 0$ ,  $\frac{1}{2}\ \frac{1}{2}\ 0$ .

**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.

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

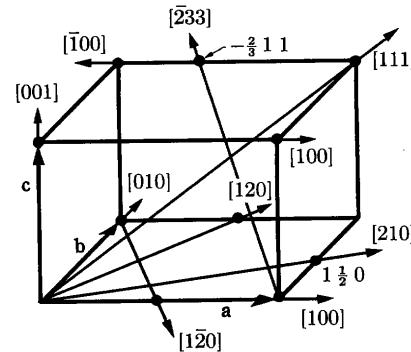


FIG. 2-8. Indices of directions.

diagonals of a cube,  $[111]$ ,  $[1\bar{1}\bar{1}]$ ,  $[\bar{1}\bar{1}1]$ , and  $[\bar{1}1\bar{1}]$ , may all be represented by the symbol  $(111)$ .

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

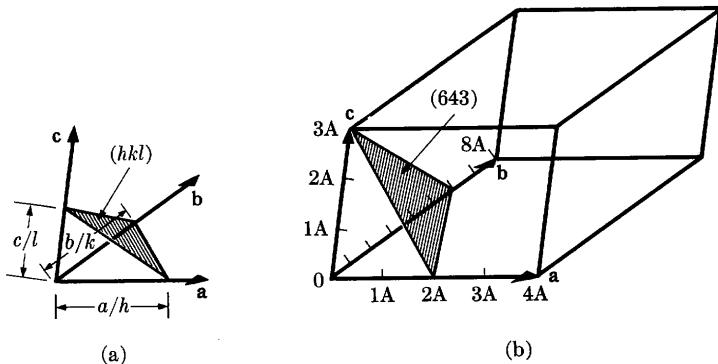


FIG. 2-9. Plane designation by Miller indices.

|                       |               |               |    |
|-----------------------|---------------|---------------|----|
| Axial lengths         | 4A            | 8A            | 3A |
| Intercept lengths     | 2A            | 6A            | 3A |
| Fractional intercepts | $\frac{1}{2}$ | $\frac{3}{4}$ | 1  |
| Miller indices        | {2}           | $\frac{4}{3}$ | 1  |
|                       | {6}           | 4             | 3  |

Miller indices are always cleared of fractions, as shown above. 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 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  $1/n$  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.

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  $120^\circ$  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

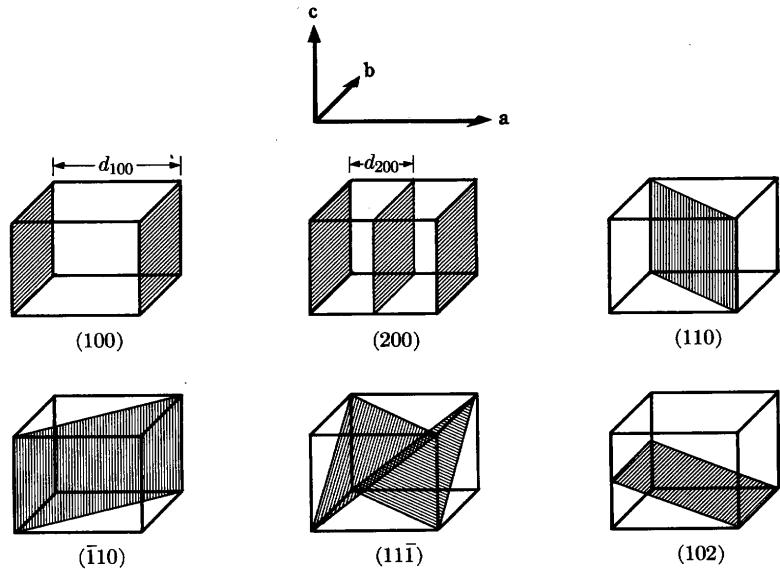


FIG. 2-10. Miller indices of lattice planes.

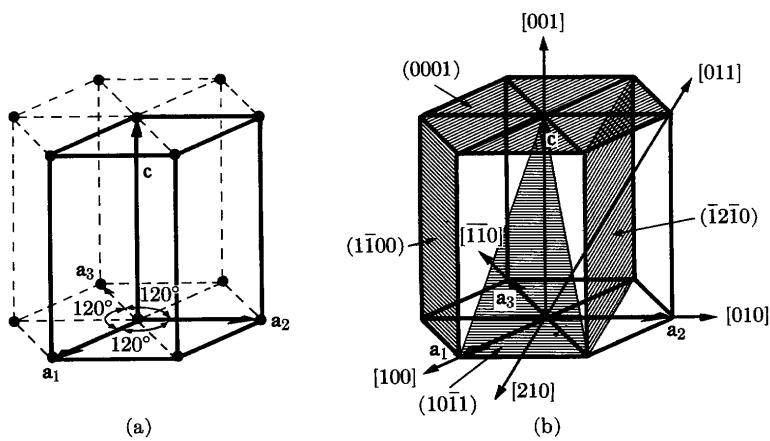


FIG. 2-11. (a) The hexagonal unit cell and (b) indices of planes and directions.

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  $(hk\cdot l)$ . 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,  $(10\cdot 0)$ ,  $(01\cdot 0)$ ,  $(\bar{1}1\cdot 0)$ ,  $(10\bar{\cdot}0)$ ,  $(0\bar{1}\cdot 0)$ ,  $(1\bar{1}\cdot 0)$  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 negative of the sum of the first two. Thus

$[100]$ , for example, becomes  $[2\bar{1}10]$ ,  $[210]$  becomes  $[10\bar{1}0]$ ,  $[010]$  becomes  $[12\bar{1}0]$ , etc.)

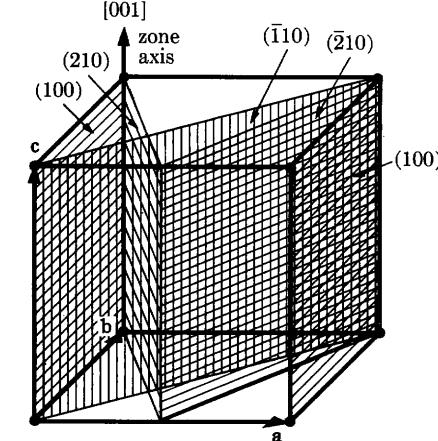
In any crystal system there are sets of equivalent lattice planes related by symmetry. These are called *planes of a form*, and the indices of any one plane, enclosed in braces  $\{hkl\}$ , stand for the whole set. In general, planes of a form have the same spacing but different Miller indices. For example, the faces of a cube,  $(100)$ ,  $(010)$ ,  $(\bar{1}00)$ ,  $(\bar{0}\bar{1}0)$ ,  $(001)$ , 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 Section 3 of Appendix 15.) 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

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

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

\* 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.

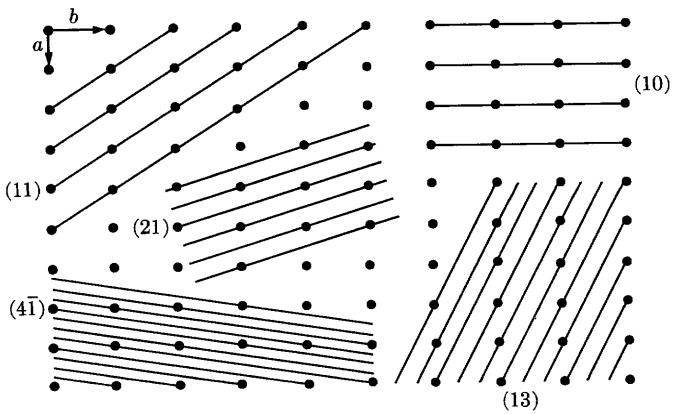


FIG. 2-13. Two-dimensional lattice, showing that lines of lowest indices have the greatest spacing and the greatest density of lattice points.

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

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

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

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

Interplanar spacing equations for all systems are given in Appendix 1.

**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 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  $\mathbf{a}_1$  and  $\mathbf{a}_2$ , 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

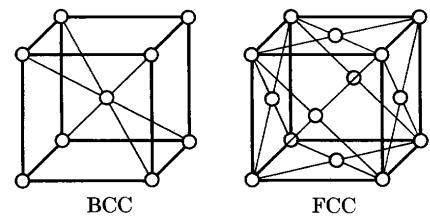
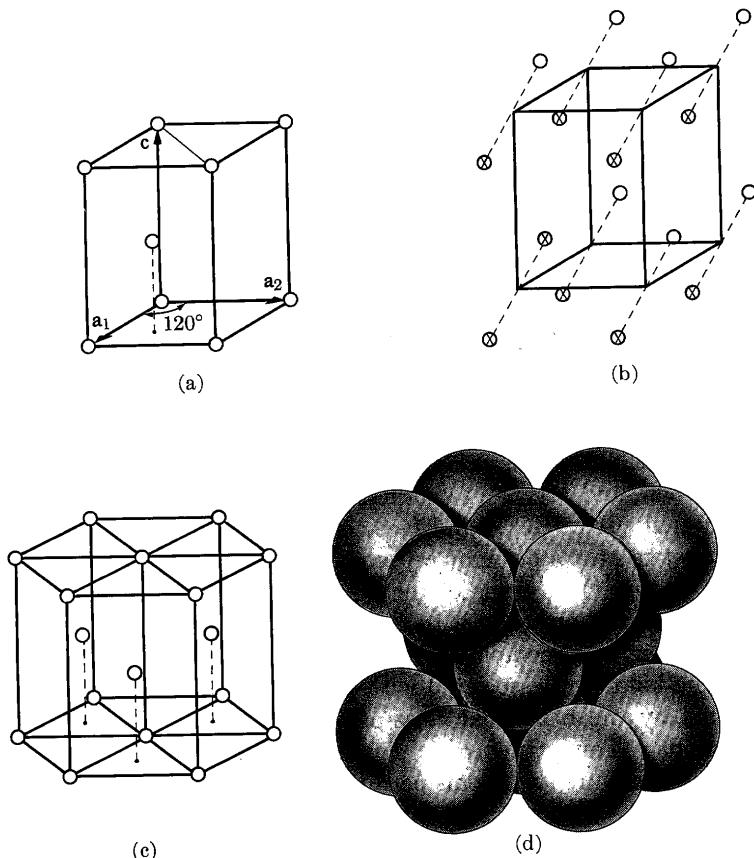


FIG. 2-14. Structures of some common metals. Body-centered cubic:  $\alpha$ -Fe, Cr, Mo, V, etc.; face-centered cubic:  $\gamma$ -Fe, Cu, Pb, Ni, etc.

FIG. 2-15. The hexagonal close-packed structure, shared by Zn, Mg, Be,  $\alpha$ -Ti, etc.

as atoms, then the resulting picture of an HCP metal is much closer to physical reality than is the relatively open 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

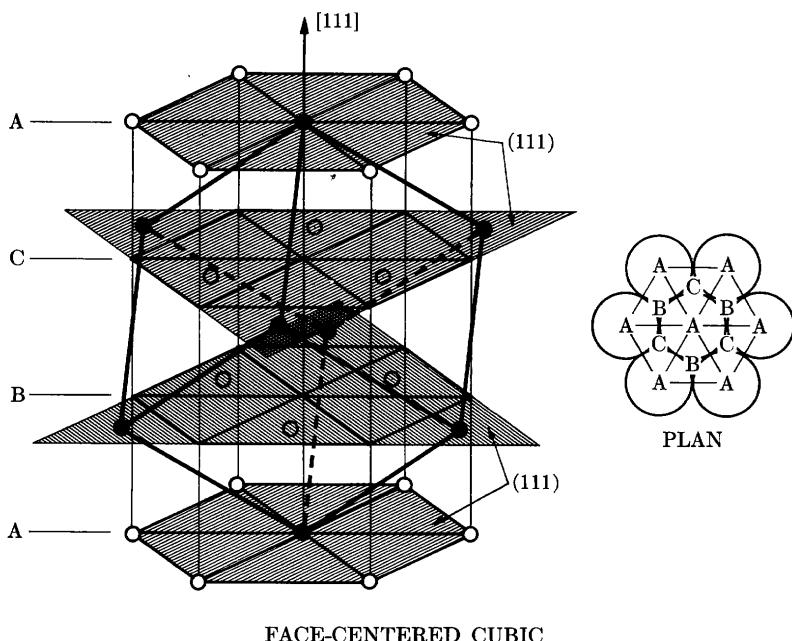


FIG. 2-16. Comparison of FCC and HCP structures.

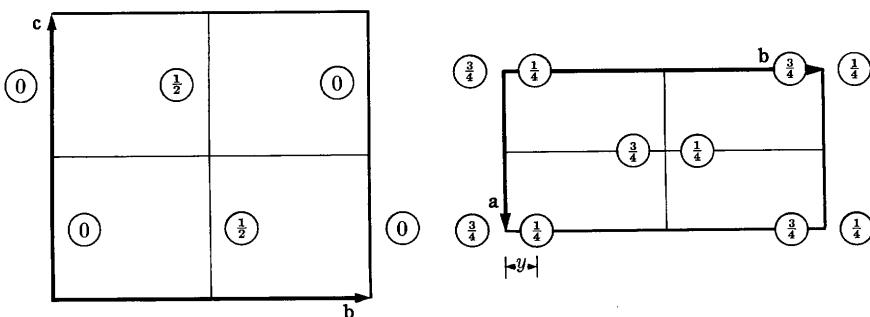


FIG. 2-17. The structure of  $\alpha$ -uranium. (C. W. Jacob and B. E. Warren, *J.A.C.S.* 59, 2588, 1937.)

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  $A B A B A B \dots$ . The first two atom layers of an FCC metal are put down in the same way, but the atoms of the third layer are placed in the hollows of the second layer and 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,  $\alpha$ -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  $0.105 \pm 0.005$ .

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 following conditions:

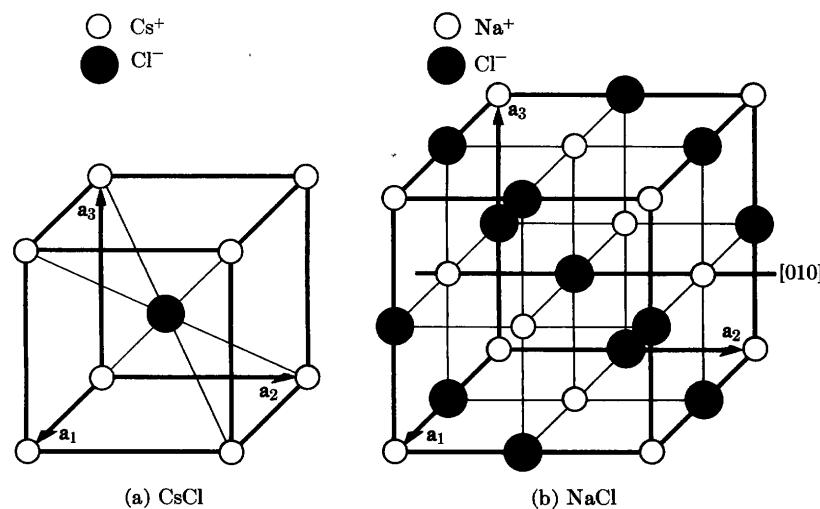


FIG. 2-18. The structures of (a) CsCl (common to CsBr, NiAl, ordered  $\beta$ -brass, ordered CuPd, etc.) and (b) NaCl (common to KCl, CaSe, PbTe, etc.).

(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 x-ray diffraction pattern of that crystal.

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:

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

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

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:

$$4 \text{Na}^+ \text{ at } 0\ 0\ 0 + \text{face-centering translations}$$

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

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),  $90^\circ$  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

$$0\ 0\ 0 + \text{face-centering translations}$$

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

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.

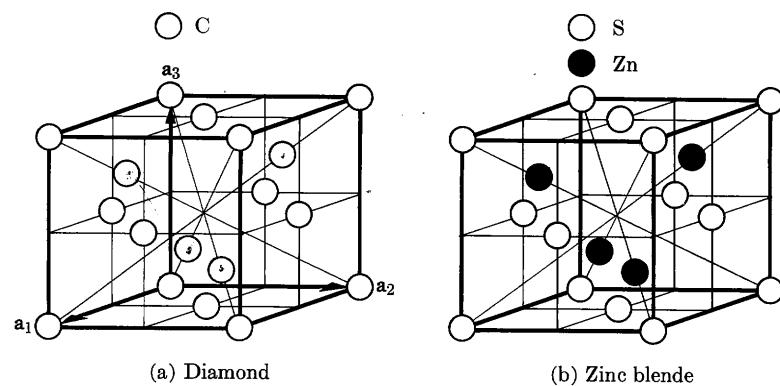


FIG. 2-19. The structures of (a) diamond (common to Si, Ge, and gray Sn) and (b) the zinc-blende form of ZnS (common to HgS, CuI, AlSb, BeSe, etc.).

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:

$$4 \text{Au at } u\ u\ u, (\frac{1}{2} + u)\ (\frac{1}{2} - u)\bar{u}, \bar{u}\ (\frac{1}{2} + u)\ (\frac{1}{2} - u), (\frac{1}{2} - u)\bar{u}\ (\frac{1}{2} + u),$$

$$4 \text{Be at }$$

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

where  $u = 0.100$  and  $w = 0.406$ , each  $\pm 0.005$ . 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.

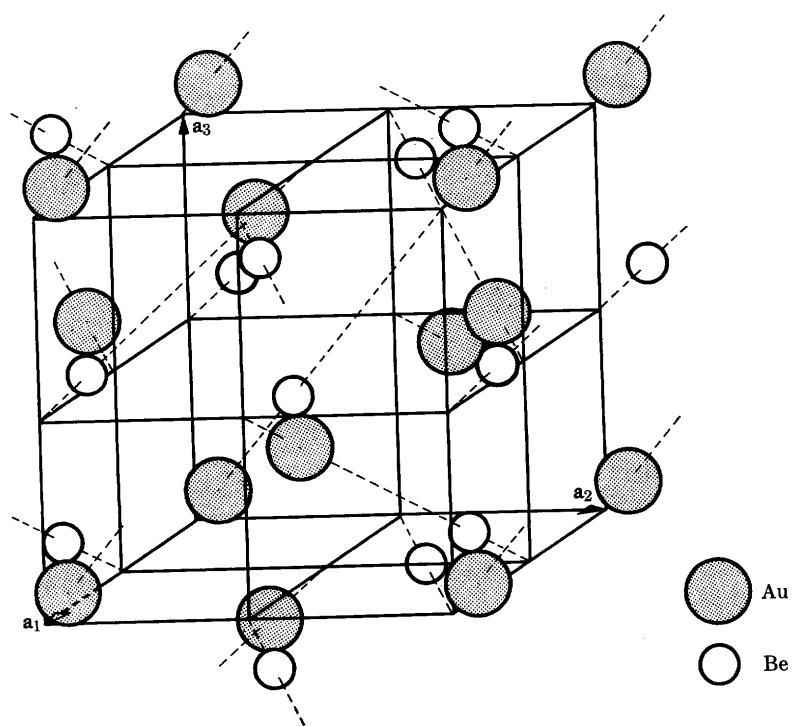


FIG. 2-20. The structure of AuBe, shared by FeSi, NiSi, CoSi, MnSi, etc. It is known as the FeSi structure. [B. D. Cullity, *Trans. A.I.M.E.* **171**, 396 (1947).]

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 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 cubic 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

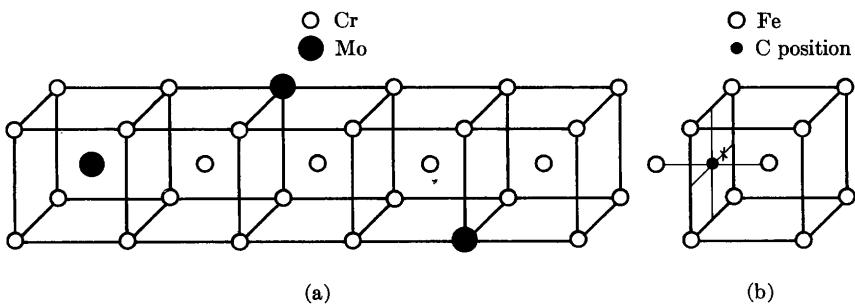


FIG. 2-21. Structure of solid solutions: (a) Mo in Cr (substitutional); (b) C in  $\alpha$ -Fe (interstitial).

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, containing a total of 29 atoms, 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  $\alpha$ -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 •) and equivalent positions in the centers of the cube faces and edges, and one at  $\frac{1}{4} 0 \frac{1}{2}$  (marked ×) 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 occu-

pied, 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 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<sub>3</sub> 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. Crystallographically, the structures of the disordered and ordered solutions are quite different; in the example cited, the structure of the former is, on the average, face-centered cubic while that of the latter 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  $\alpha$ -iron is 2.87A, 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  $(\sqrt{3}/2)a = 2.48$ A. The following formulas give

\* 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.

the distance of closest approach in the three common metal structures:

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

Values of the distance of closest approach, together with the crystal structures and lattice parameters of the elements, are tabulated in Appendix 13.

To a first approximation, the size of an atom is a constant. In other words, an iron atom has 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 in diamond cubic 4. The smaller the coordination number, the smaller the volume occupied by a given atom, and the amount of contraction to be expected with decrease in coordination number is found to be:

| Change in coordination | Size contraction, percent |
|------------------------|---------------------------|
| 12 → 8                 | 3                         |
| 12 → 6                 | 4                         |
| 12 → 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  $\alpha$ -iron. If it were dissolved in copper, its diameter would be approximately 2.48/0.97, or 2.56A.

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<sup>++</sup>, Fe<sup>+++</sup> have diameters of 2.48, 1.66, and 1.34A, respectively.

**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}, {1100}, {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 recrystallization, 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.

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 (a) 180° rotation about an axis, called the twin axis, or (b) 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,  $\alpha$ -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 ( $\alpha$ -Fe, W, etc.).

**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 {111}. 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. 2-22(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. 2-22(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.

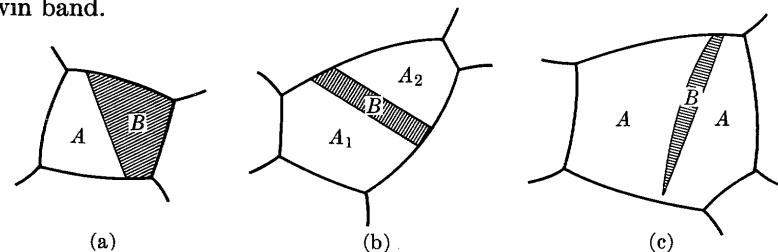


FIG. 2-22. Twinned grains: (a) and (b) FCC annealing twins; (c) HCP deformation twin.

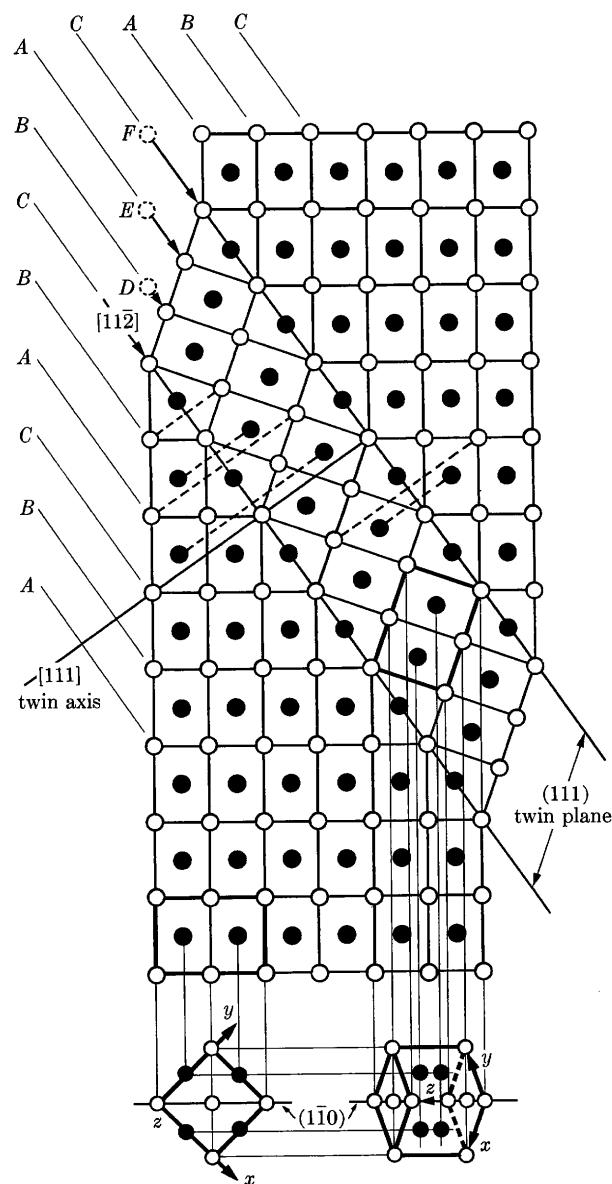
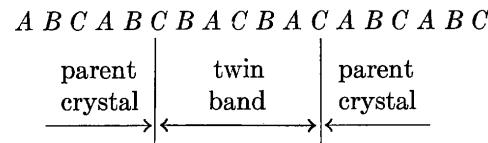
FIG. 2-23. Twin band in FCC lattice. Plane of main drawing is  $(1\bar{1}0)$ .

Figure 2-23 illustrates the structure of an FCC twin band. The plane of the main drawing is  $(1\bar{1}0)$ , the  $(111)$  twin plane is perpendicular to this plane, and the  $[111]$  twin axis lies in it. Open circles represent atoms in the plane of the drawing and filled circles those in the layers immediately above or below. The reflection symmetry across the twin plane is suggested by the dashed lines connecting several pairs of atoms.

The statement that a rotation twin of this kind is related to the parent crystal by a  $180^\circ$  rotation about the twin axis is merely an expression of the orientation relationship between the two and is not meant to suggest that a twin is formed by a physical rotation of one part of the crystal with respect to another. Actually, FCC annealing twins are formed by a change in the normal growth mechanism. Suppose that, during normal grain growth following recrystallization, a grain boundary is roughly parallel to  $(111)$  and is advancing in a direction approximately normal to this boundary, namely  $[111]$ . To say that the boundary is advancing is to say that atoms are leaving the lattice of the consumed grain and joining that of the growing grain. The grain is therefore growing by the addition of layers of atoms parallel to  $(111)$ , and we already know that these layers are piled up in the sequence  $A\ B\ C\ A\ B\ C\dots$  in an FCC crystal. If, however, a mistake should occur and this sequence become altered to  $C\ B\ A\ C\ B\ A\dots$ , the crystal so formed would still be FCC but it would be a twin of the former. If a similar mistake occurred later, a crystal of the original orientation would start growing and a twin band would be formed. With this symbolism, we may indicate a twin band as follows:



In this terminology, the symbols themselves are imaged in the mirror  $C$ , the twin plane. At the left of Fig. 2-23 the positional symbols  $A$ ,  $B$ ,  $C$  are attached to various  $(111)$  planes to show the change in stacking which occurs at the boundaries of the twin band. Parenthetically, it should be remarked that twin bands visible under the light microscope are thousands of times thicker than the one shown in this drawing.

There is still another way of *describing* the orientation relationship between an FCC crystal and its twin: the  $(111)$  layers of the twin are in positions which would result from homogeneous shear in a  $[11\bar{2}]$  direction, each layer moving by an amount proportional to its distance from the twin plane. In Fig. 2-23, this shear is indicated by the arrows going from initial positions  $D$ ,  $E$ ,  $F$  to final positions in the twin. Although it has been frequently suggested that such twins are *formed* by deformation, no

convincing evidence for this view has been advanced and it is generally held that annealing twins are the result of the growth process described above. Nevertheless, this hypothetical shear is sometimes a useful way of describing the orientation relationship between a crystal and its twin.

**Deformation twins** are found in both BCC and HCP lattices and are all that their name implies, since, in both cases, the cause of twinning is deformation. In each case, the orientation relationship between parent crystal and twin is that of reflection across a plane.

In BCC structures, the twin plane is  $\{112\}$  and the twinning shear is in the direction  $[11\bar{1}]$ . The only common example of such twins is in  $\alpha$ -iron (ferrite) deformed by impact, where they occur as extremely narrow twin bands called Neumann bands. It should be noted that, in cubic lattices, both  $\{112\}$  and  $\{111\}$  reflection twinning produce the same orientation relationship; however, they differ in the interatomic distances produced, and an FCC lattice can twin by reflection on  $\{111\}$  with less distortion than on  $\{112\}$ , while for the same reason  $\{112\}$  is the preferred plane for BCC lattices.

In HCP metals, the twin plane is normally  $(10\bar{1}2)$ . The twinning shear is not well understood; in a gross sense, it takes place in the direction  $[\bar{2}\bar{1}1]$  for metals with  $c/a$  ratios less than  $\sqrt{3}$  (Be, Ti, Mg) and in the reverse direction  $[2\bar{1}\bar{1}]$  for metals with  $c/a$  larger than  $\sqrt{3}$  (Zn, Cd), but the direction of motion of individual atoms during shear is not definitely known. Figure 2-22(c) illustrates the usual form of a twin band in HCP metals, and it will be noted that the composition "plane," although probably parallel or nearly parallel to the twin plane, is not quite flat but often exhibits appreciable curvature. Figure 2-24 shows the structure of a twin band in cadmium ( $c/a = 1.886$ ). The twin plane is perpendicular to the plane of the drawing ( $\bar{1}2\bar{1}0$ ), and the shear direction lies in it. Open and filled circles represent atoms in and immediately above or below this plane, respectively. While the over-all shear is not very large (0.17 for cadmium), it produces a drastic reorientation of the lattice, the  $c$  axis of the twin being almost at right angles to the  $c$  axis of the parent crystal. It is for this reason, incidentally, that slip in HCP metals is promoted by twinning; if a crystal is unfavorably oriented for slip on its basal planes, then the occurrence of twinning will produce a favorable orientation of the basal planes in the twinned part.

Twins, in general, can form on different planes in the same crystal. For example, there are four  $\{111\}$  planes of different orientation on which twinning can take place in an FCC crystal. Accordingly, in the microstructure of recrystallized copper, for example, one often sees twin bands running in more than one direction in the same grain.

A crystal may also twin repeatedly, producing several new orientations. If crystal  $A$  twins to form  $B$ , which twins to form  $C$ , etc., then  $B$ ,  $C$ , etc.,

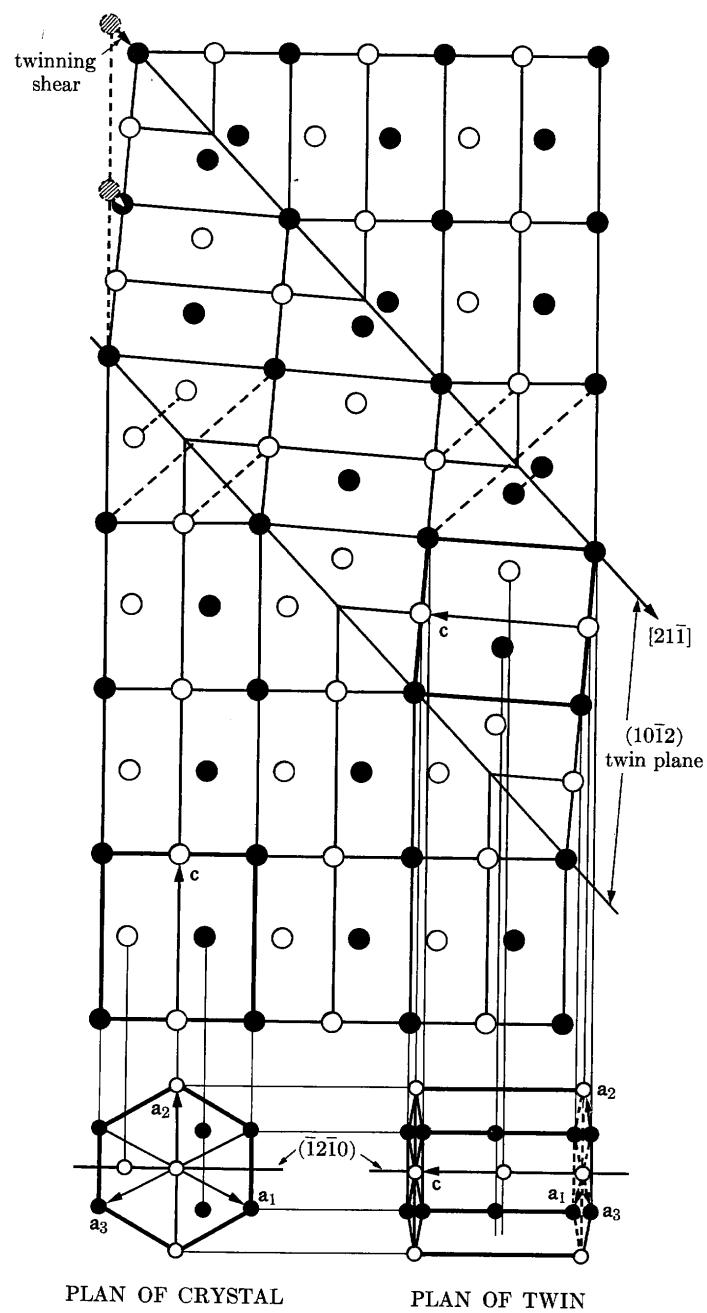


FIG. 2-24. Twin band in HCP lattice. Plane of main drawing is  $(\bar{1}2\bar{1}0)$ .

are said to be first-order, second-order, etc., twins of the parent crystal  $A$ . Not all these orientations are new. In Fig. 2-22(b), for example,  $B$  may be regarded as the first-order twin of  $A_1$ , and  $A_2$  as the first order twin of  $B$ .  $A_2$  is therefore the second-order twin of  $A_1$  but has the same orientation as  $A_1$ .

**2-11 The stereographic projection.** Crystal drawings made in perspective or in the form of plan and elevation, while they have their uses, are not suitable for displaying the angular relationship between lattice planes and directions. But frequently we are more interested in these angular relationships than in any other aspect of the crystal, and we then need a kind of drawing on which the angles between planes can be accurately measured and which will permit graphical solution of problems involving such angles. The stereographic projection fills this need.

The orientation of any plane in a crystal can be just as well represented by the inclination of the normal to that plane relative to some reference plane as by the inclination of the plane itself. All the planes in a crystal can thus be represented by a set of plane normals radiating from some one point within the crystal. If a reference sphere is now described about this point, the plane normals will intersect the surface of the sphere in a set of points called *poles*. This procedure is illustrated in Fig. 2-25, which is restricted to the  $\{100\}$  planes of a cubic crystal. The pole of a plane represents, by its position on the sphere, the orientation of that plane.

A plane may also be represented by the trace the extended plane makes in the surface of the sphere, as illustrated in Fig. 2-26, where the trace  $ABCDA$  represents the plane whose pole is  $P_1$ . This trace is a *great circle*, i.e., a circle of maximum diameter, if the plane passes through the center of the sphere. A plane not passing through the center will intersect the sphere in a *small circle*. On a ruled globe, for example, the longitude lines

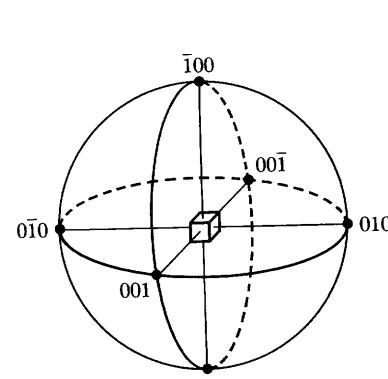


FIG. 2-25.  $\{100\}$  poles of a cubic crystal.

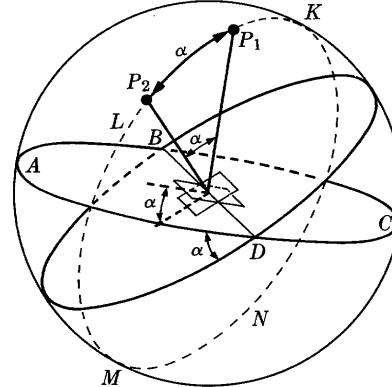


FIG. 2-26. Angle between two planes.

(meridians) are great circles, while the latitude lines, except the equator, are small circles.

The angle  $\alpha$  between two planes is evidently equal to the angle between their great circles or to the angle between their normals (Fig. 2-26). But this angle, in degrees, can also be measured on the surface of the sphere along the great circle  $KLMNK$  connecting the poles  $P_1$  and  $P_2$  of the two planes, if this circle has been divided into 360 equal parts. The measurement of an angle has thus been transferred from the planes themselves to the surface of the reference sphere.

Preferring, however, to measure angles on a flat sheet of paper rather than on the surface of a sphere, we find ourselves in the position of the

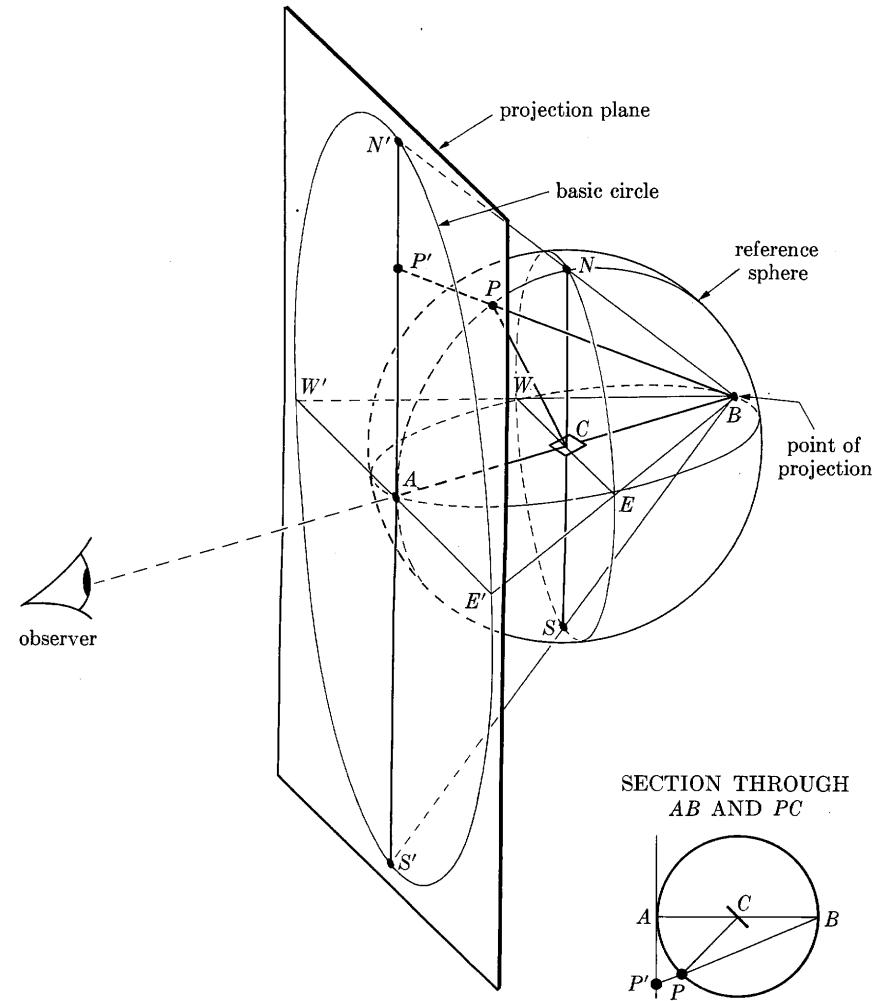


FIG. 2-27. The stereographic projection.

geographer who wants to transfer a map of the world from a globe to a page of an atlas. Of the many known kinds of projections, he usually chooses a more or less equal-area projection so that countries of equal area will be represented by equal areas on the map. In crystallography, however, we prefer the equiangular stereographic projection since it preserves angular relationships faithfully although distorting areas. It is made by placing a plane of projection normal to the end of any chosen diameter of the sphere and using the other end of that diameter as the point of projection. In Fig. 2-27 the projection plane is normal to the diameter  $AB$ , and the projection is made from the point  $B$ . If a plane has its pole at  $P$ , then the stereographic projection of  $P$  is at  $P'$ , obtained by drawing the line  $BP$  and producing it until it meets the projection plane. Alternately stated, the stereographic projection of the pole  $P$  is the shadow cast by  $P$  on the projection plane when a light source is placed at  $B$ . The observer, incidentally, views the projection from the side opposite the light source.

The plane  $NESW$  is normal to  $AB$  and passes through the center  $C$ . It therefore cuts the sphere in half and its trace in the sphere is a great circle. This great circle projects to form the *basic circle*  $N'E'S'W'$  on the projection, and all poles on the left-hand hemisphere will project within this basic circle. Poles on the right-hand hemisphere will project outside this basic circle, and those near  $B$  will have projections lying at very large distances from the center. If we wish to plot such poles, we move the point of projection to  $A$  and the projection plane to  $B$  and distinguish the new set of points so formed by minus signs, the previous set (projected from  $B$ ) being marked with plus signs. Note that movement of the projection plane along  $AB$  or its extension merely alters the magnification; we usually make it tangent to the sphere, as illustrated, but we can also make it pass through the center of the sphere, for example, in which case the basic circle becomes identical with the great circle  $NESW$ .

A lattice plane in a crystal is several steps removed from its stereographic projection, and it may be worth-while at this stage to summarize these steps:

- (1) The plane  $C$  is represented by its normal  $CP$ .
- (2) The normal  $CP$  is represented by its pole  $P$ , which is its intersection with the reference sphere.
- (3) The pole  $P$  is represented by its stereographic projection  $P'$ .

After gaining some familiarity with the stereographic projection, the student will be able mentally to omit these intermediate steps and he will then refer to the projected point  $P'$  as the pole of the plane  $C$  or, even more directly, as the plane  $C$  itself.

*Great circles* on the reference sphere project as circular arcs on the projection or, if they pass through the points  $A$  and  $B$  (Fig. 2-28), as straight

lines through the center of the projection. Projected great circles always cut the basic circle in diametrically opposite points, since the locus of a great circle on the sphere is a set of diametrically opposite points. Thus the great circle  $ANBS$  in Fig. 2-28 projects as the straight line  $N'S'$  and  $AWBE$  as  $W'E'$ ; the great circle  $NGSH$ , which is inclined to the plane of projection, projects as the circle arc  $N'G'S'$ . If the half great circle  $WAE$  is divided into 18 equal parts and these points of division projected on  $W'A'E'$ , we obtain a graduated scale, at  $10^\circ$  intervals, on the equator of the basic circle.

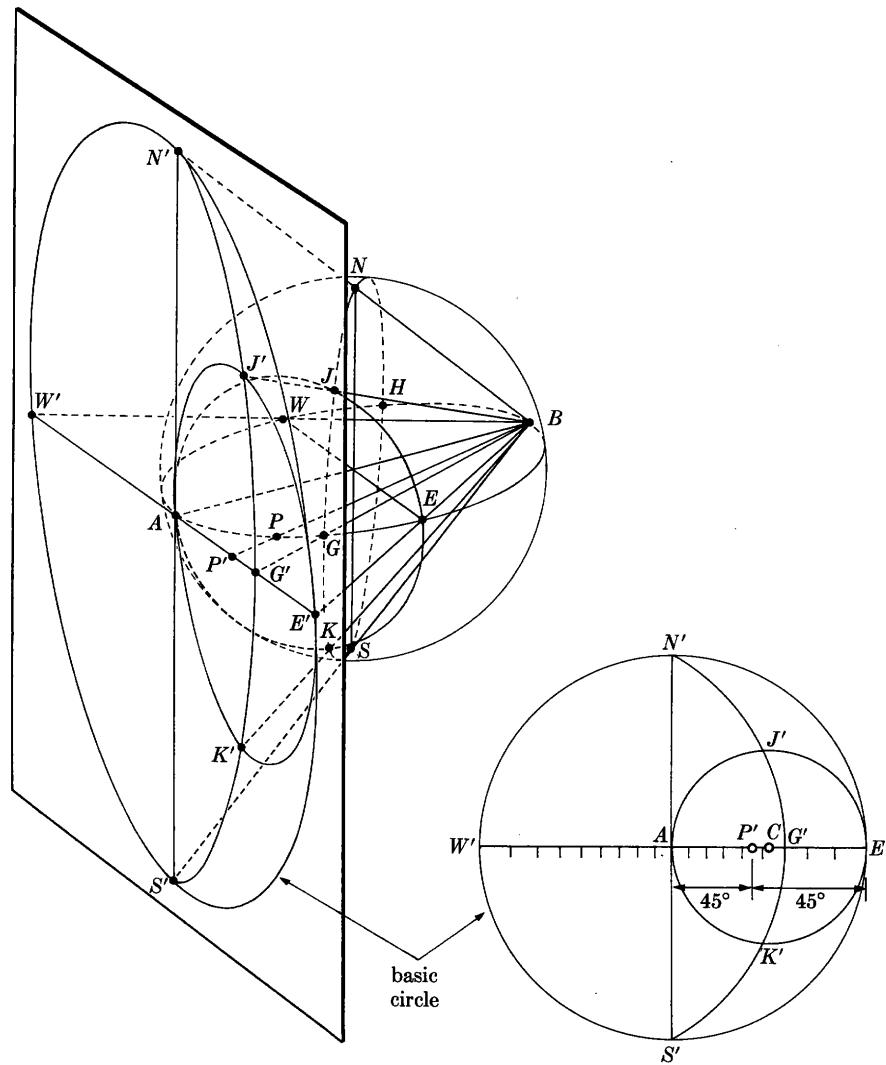


FIG. 2-28. Stereographic projection of great and small circles.

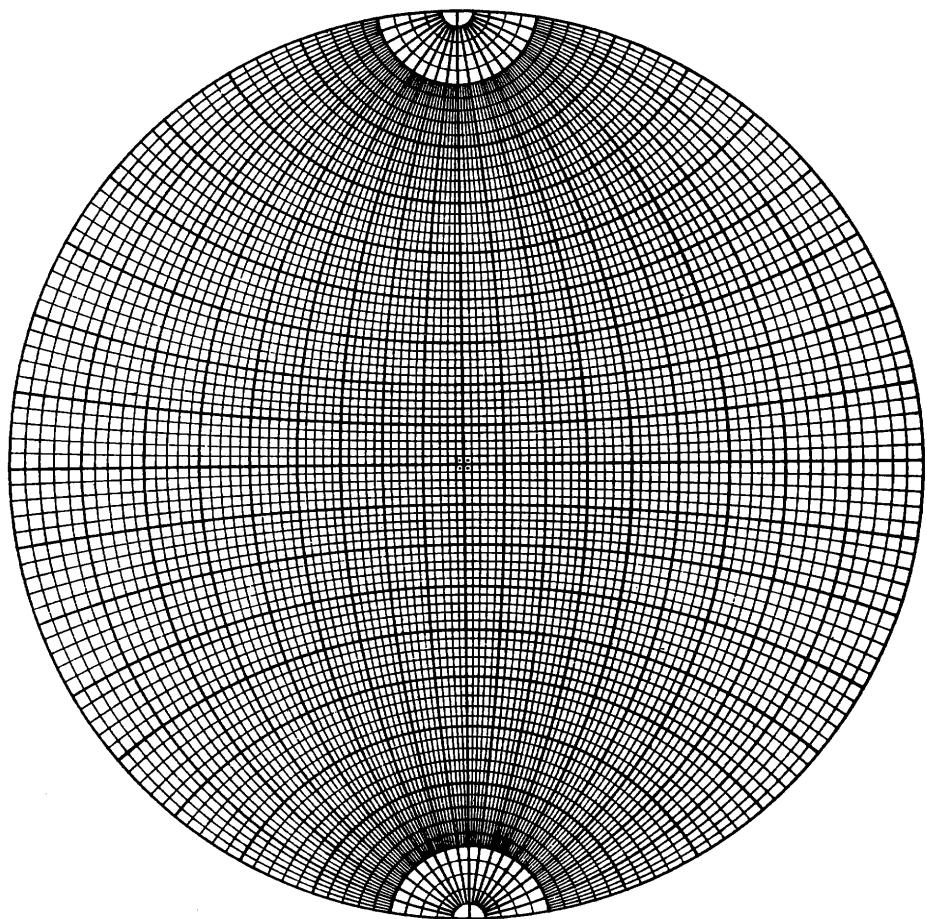


FIG. 2-29. Wulff net drawn to  $2^\circ$  intervals.

*Small circles* on the sphere also project as circles, but their projected center does not coincide with their center on the projection. For example, the circle  $AJEK$  whose center  $P$  lies on  $AWBE$  projects as  $AJ'E'K'$ . Its center *on the projection* is at  $C$ , located at equal distances from  $A$  and  $E'$ , but its *projected center* is at  $P'$ , located an equal number of degrees ( $45^\circ$  in this case) from  $A$  and  $E'$ .

The device most useful in solving problems involving the stereographic projection is the *Wulff net* shown in Fig. 2-29. It is the projection of a sphere ruled with parallels of latitude and longitude on a plane parallel to the north-south axis of the sphere. The latitude lines on a Wulff net are small circles extending from side to side and the longitude lines (meridians) are great circles connecting the north and south poles of the net.

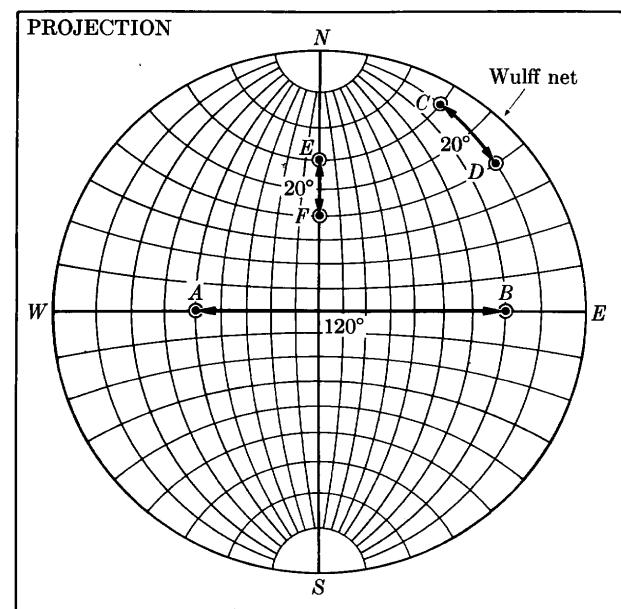


FIG. 2-30. Stereographic projection superimposed on Wulff net for measurement of angle between poles.

These nets are available in various sizes, one of 18-cm diameter giving an accuracy of about one degree, which is satisfactory for most problems; to obtain greater precision, either a larger net or mathematical calculation must be used. Wulff nets are used by making the stereographic projection on tracing paper and with the basic circle of the same diameter as that of the Wulff net; the projection is then superimposed on the Wulff net and pinned at the center so that it is free to rotate with respect to the net.

To return to our problem of the measurement of the angle between two crystal planes, we saw in Fig. 2-26 that this angle could be measured on the surface of the sphere along the great circle connecting the poles of the two planes. This measurement can also be carried out on the stereographic projection *if, and only if, the projected poles lie on a great circle*. In Fig. 2-30, for example, the angle between the planes\*  $A$  and  $B$  or  $C$  and  $D$  can be measured directly, simply by counting the number of degrees separating them along the great circle on which they lie. Note that the angle  $C-D$  equals the angle  $E-F$ , there being the same difference in latitude between  $C$  and  $D$  as between  $E$  and  $F$ .

If the two poles do not lie on a great circle, then the projection is rotated relative to the Wulff net until they do lie on a great circle, where the de-

\* We are here using the abbreviated terminology referred to above.

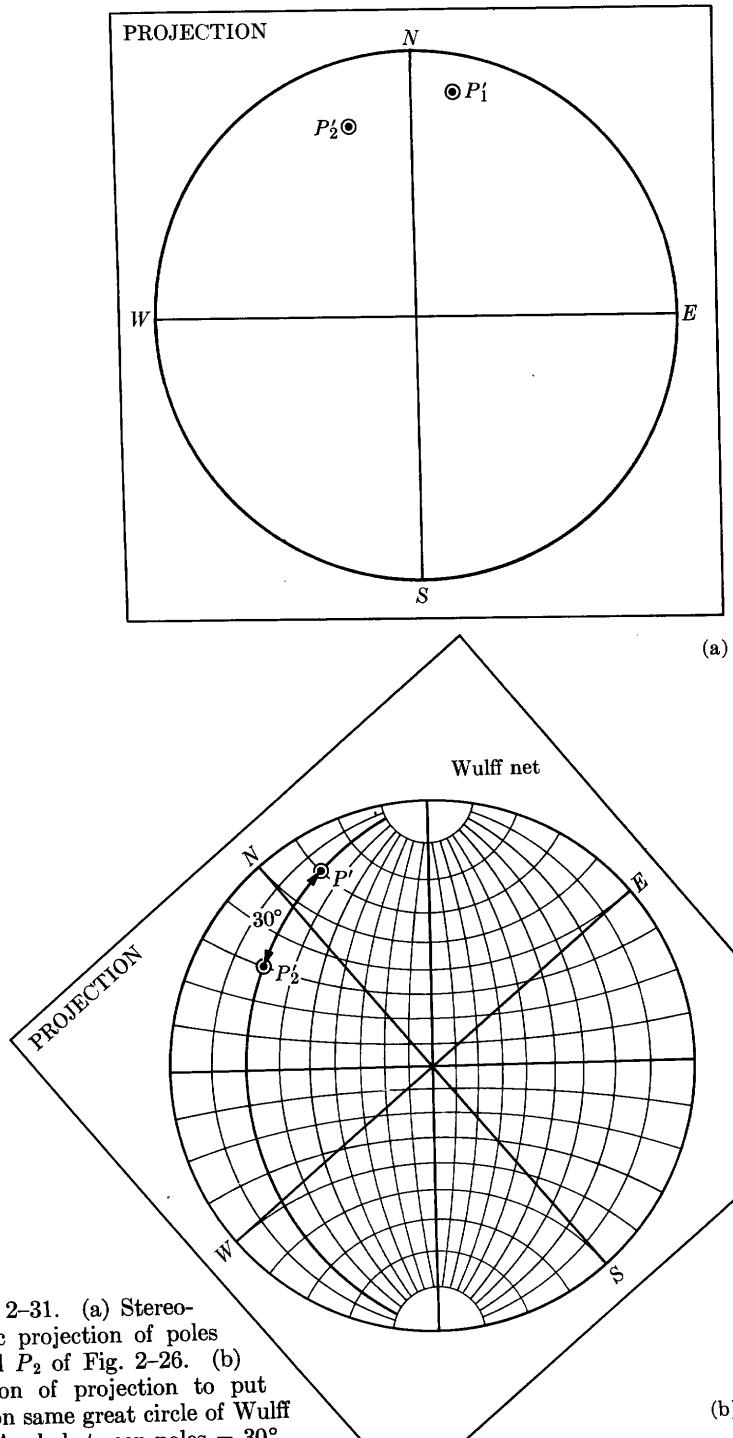


FIG. 2-31. (a) Stereographic projection of poles  $P_1$  and  $P_2$  of Fig. 2-26. (b) Rotation of projection to put poles on same great circle of Wulff net. Angle between poles =  $30^\circ$ .

sired angle measurement can then be made. Figure 2-31(a) is a projection of the two poles  $P_1$  and  $P_2$  shown in perspective in Fig. 2-26, and the angle between them is found by the rotation illustrated in Fig. 2-31(b). This rotation of the projection is equivalent to rotation of the poles on latitude circles of a sphere whose north-south axis is perpendicular to the projection plane.

As shown in Fig. 2-26, a plane may be represented by its trace in the reference sphere. This trace becomes a great circle in the stereographic projection. Since every point on this great circle is  $90^\circ$  from the pole of the plane, the great circle may be found by rotating the projection until the pole falls on the equator of the underlying Wulff net and tracing that meridian which cuts the equator  $90^\circ$  from the pole, as illustrated in Fig. 2-32. If this is done for two poles, as in Fig. 2-33, the angle between the corresponding planes may also be found from the angle of intersection of the two great circles corresponding to these poles; it is in this sense that the stereographic projection is said to be angle-true. This method of angle measurement is not as accurate, however, as that shown in Fig. 2-31(b).

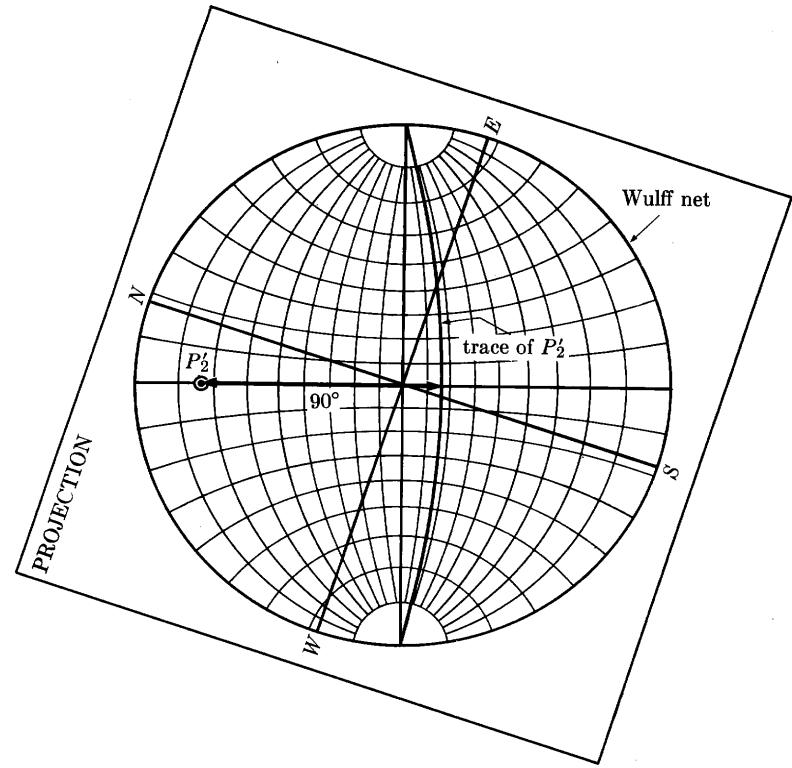


FIG. 2-32. Method of finding the trace of a pole (the pole  $P_2'$  in Fig. 2-31).

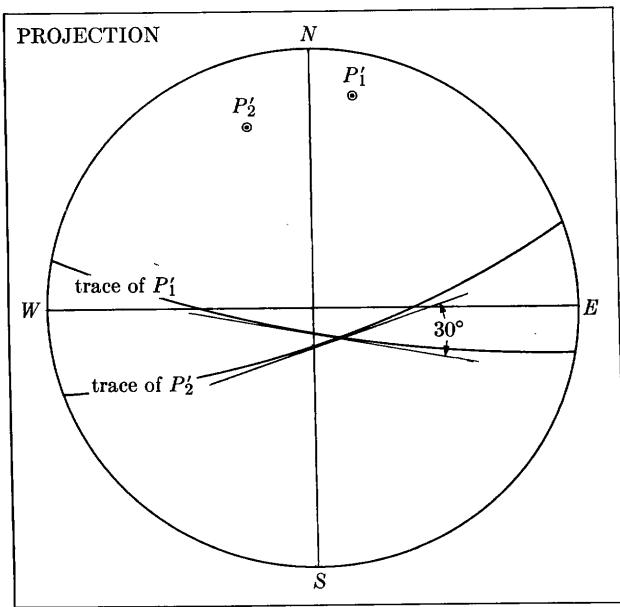


FIG. 2-33. Measurement of an angle between two poles ( $P_1$  and  $P_2$  of Fig. 2-26) by measurement of the angle of intersection of the corresponding traces.

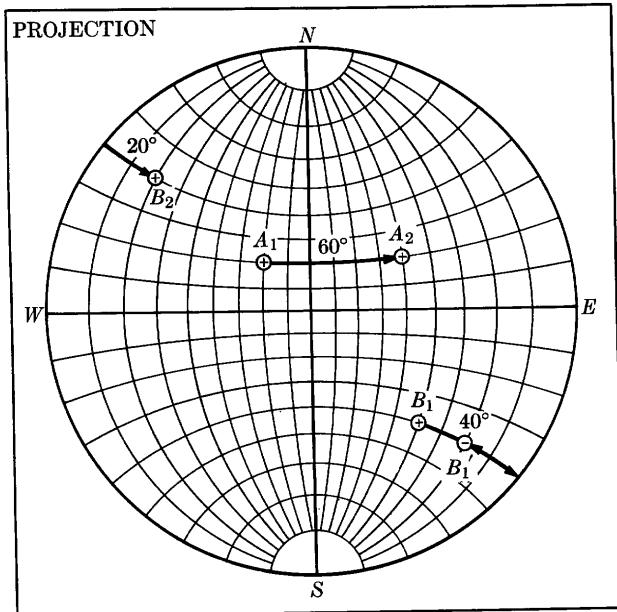


FIG. 2-34. Rotation of poles about *NS* axis of projection.

We often wish to rotate poles around various axes. We have already seen that rotation about an axis normal to the projection is accomplished simply by rotation of the projection around the center of the Wulff net. Rotation about an axis lying in the plane of the projection is performed by, first, rotating the *axis* about the center of the Wulff net until it coincides with the north-south axis if it does not already do so, and, second, moving the poles involved along their respective latitude circles the required number of degrees. Suppose it is required to rotate the poles  $A_1$  and  $B_1$  shown in Fig. 2-34 by  $60^\circ$  about the *NS* axis, the direction of motion being from *W* to *E* on the projection. Then  $A_1$  moves to  $A_2$  along its latitude circle as shown.  $B_1$ , however, can rotate only  $40^\circ$  before finding itself at the edge of the projection; we must then imagine it to move  $20^\circ$  in from the edge to the point  $B'_1$  on the other side of the projection, staying always on its own latitude circle. The final position of this pole on the positive side of the projection is at  $B_2$  diametrically opposite  $B'_1$ .

Rotation about an axis inclined to the plane of projection is accomplished by compounding rotations about axes lying in and perpendicular to the projection plane. In this case, the given axis must first be rotated into coincidence with one or the other of the two latter axes, the given rotation performed, and the axis then rotated back to its original position. Any movement of the given axis must be accompanied by a similar movement of all the poles on the projection.

For example, we may be required to rotate  $A_1$  about  $B_1$  by  $40^\circ$  in a clockwise direction (Fig. 2-35). In (a) the pole to be rotated  $A_1$  and the rotation axis  $B_1$  are shown in their initial position. In (b) the projection has been rotated to bring  $B_1$  to the equator of a Wulff net. A rotation of  $48^\circ$  about the *NS* axis of the net brings  $B_1$  to the point  $B_2$  at the center of the net; at the same time  $A_1$  must go to  $A_2$  along a parallel of latitude. The rotation axis is now perpendicular to the projection plane, and the required rotation of  $40^\circ$  brings  $A_2$  to  $A_3$  along a circular path centered on  $B_2$ . The operations which brought  $B_1$  to  $B_2$  must now be reversed in order to return  $B_2$  to its original position. Accordingly,  $B_2$  is brought to  $B_3$  and  $A_3$  to  $A_4$ , by a  $48^\circ$  reverse rotation about the *NS* axis of the net. In (c) the projection has been rotated back to its initial position, construction lines have been omitted, and only the initial and final positions of the rotated pole are shown. During its rotation about  $B_1$ ,  $A_1$  moves along the small circle shown. This circle is centered at  $C$  on the projection and not at its projected center  $B_1$ . To find  $C$  we use the fact that all points on the circle must lie at equal *angular* distances from  $B_1$ ; in this case, measurement on a Wulff net shows that both  $A_1$  and  $A_4$  are  $76^\circ$  from  $B_1$ . Accordingly, we locate any other point, such as  $D$ , which is  $76^\circ$  from  $B_1$ , and knowing three points on the required circle, we can locate its center  $C$ .

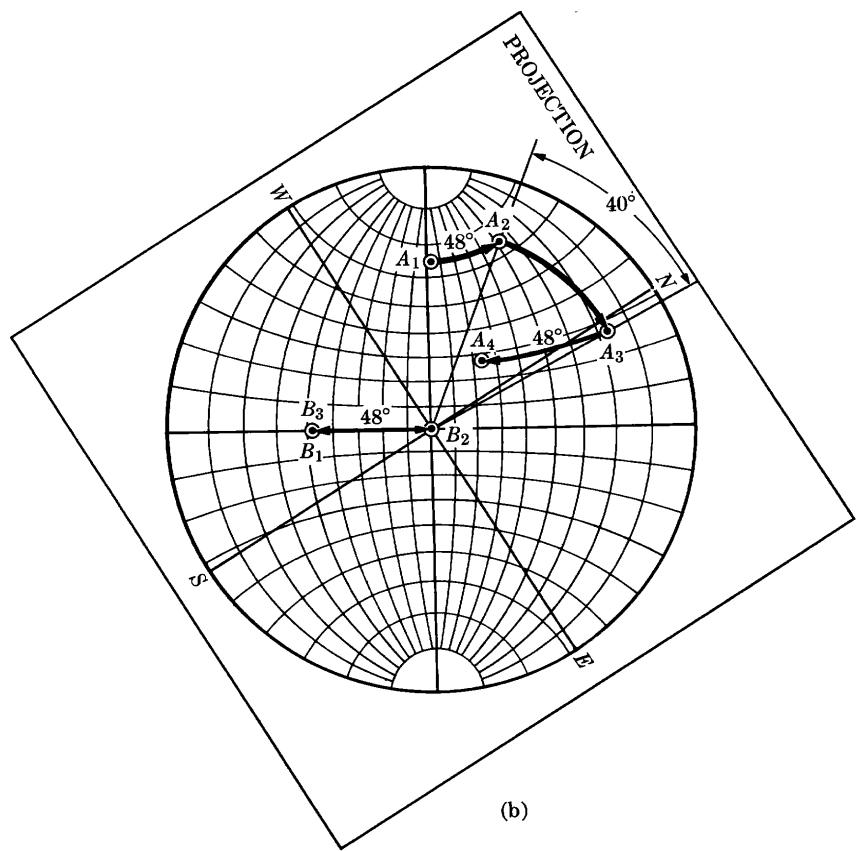


FIG. 2-35. Rotation of a pole about an inclined axis.

In dealing with problems of crystal orientation a *standard projection* is of very great value, since it shows at a glance the relative orientation of all the important planes in the crystal. Such a projection is made by selecting some important crystal plane of low indices as the plane of projection [e.g., (100), (110), (111), or (0001)] and projecting the poles of various crystal planes onto the selected plane. The construction of a standard projection of a crystal requires a knowledge of the interplanar angles for all the principal planes of the crystal. A set of values applicable to all crystals in the cubic system is given in Table 2-3, but those for crystals of other systems depend on the particular axial ratios involved and must be calculated for each case by the equations given in Appendix 1. Much time can be saved in making standard projections by making use of the zonal relation: the normals to all planes belonging to one zone are coplanar and at right angles to the zone axis. Consequently, the poles of planes of a zone will all lie on the same great circle on the projection, and the axis of the zone will be at  $90^\circ$  from this great circle. Furthermore, important planes usually belong to more than one zone and their poles are therefore located at the intersection of zone circles. It is also helpful to remember that important directions, which in the cubic system are normal to planes of the same indices, are usually the axes of important zones.

Figure 2-36(a) shows the principal poles of a cubic crystal projected on the (001) plane of the crystal or, in other words, a standard (001) projection. The location of the {100} cube poles follows immediately from Fig. 2-25. To locate the {110} poles we first note from Table 2-3 that they must lie at  $45^\circ$  from {100} poles, which are themselves  $90^\circ$  apart. In

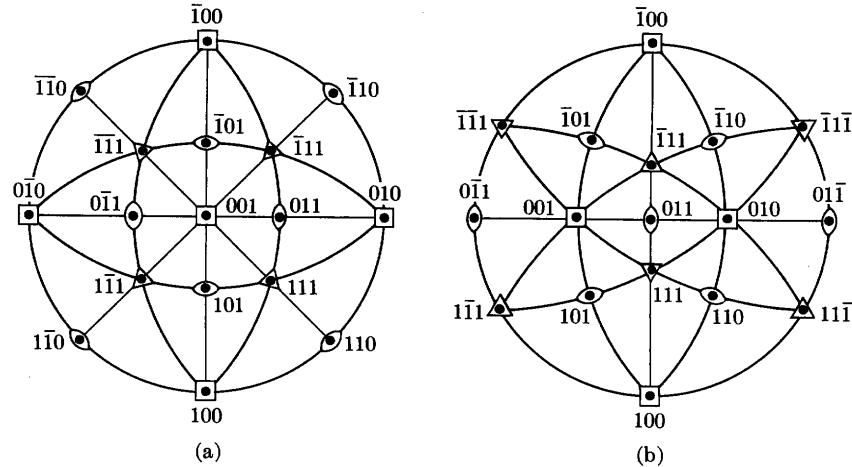


FIG. 2-36. Standard projections of cubic crystals, (a) on (001) and (b) on (011).

TABLE 2-3

INTERPLANAR ANGLES (IN DEGREES) IN CUBIC CRYSTALS BETWEEN  
PLANES OF THE FORM  $\{h_1 k_1 l_1\}$  AND  $\{h_2 k_2 l_2\}$

| $\{h_2 k_2 l_2\}$ | $\{h_1 k_1 l_1\}$ |      |      |      |      |      |      |
|-------------------|-------------------|------|------|------|------|------|------|
|                   | 100               | 110  | 111  | 210  | 211  | 221  | 310  |
| 100               | 0                 |      |      |      |      |      |      |
|                   | 90                |      |      |      |      |      |      |
| 110               | 45                | 0    |      |      |      |      |      |
|                   | 90                | 60   |      |      |      |      |      |
| 111               | 54.7              | 35.3 | 0    |      |      |      |      |
|                   |                   | 90   | 70.5 |      |      |      |      |
| 210               | 26.6              | 18.4 | 39.2 | 0    |      |      |      |
|                   | 63.4              | 50.8 | 75.0 | 36.9 |      |      |      |
|                   | 90                | 71.6 |      | 53.1 |      |      |      |
| 211               | 35.3              | 30   | 19.5 | 24.1 | 0    |      |      |
|                   | 65.9              | 54.7 | 61.9 | 43.1 | 33.6 |      |      |
|                   |                   | 73.2 | 90   | 56.8 | 48.2 |      |      |
|                   |                   |      | 90   |      |      |      |      |
| 221               | 48.2              | 19.5 | 15.8 | 26.6 | 17.7 | 0    |      |
|                   | 70.5              | 45   | 54.7 | 41.8 | 35.3 | 27.3 |      |
|                   |                   | 76.4 | 78.9 | 53.4 | 47.1 | 39.0 |      |
|                   |                   |      | 90   |      |      |      |      |
| 310               | 18.4              | 26.6 | 43.1 | 8.1  | 25.4 | 32.5 | 0    |
|                   | 71.6              | 47.9 | 68.6 | 58.1 | 49.8 | 42.5 | 25.9 |
|                   |                   | 90   | 63.4 |      | 45   | 58.9 | 36.9 |
|                   |                   |      | 77.1 |      |      |      |      |
| 311               | 25.2              | 31.5 | 29.5 | 19.3 | 10.0 | 25.2 | 17.6 |
|                   | 72.5              | 64.8 | 58.5 | 47.6 | 42.4 | 45.3 | 40.3 |
|                   |                   | 90   | 80.0 | 66.1 | 60.5 | 59.8 | 55.1 |
| 320               | 33.7              | 11.3 | 61.3 | 7.1  | 25.2 | 22.4 | 15.3 |
|                   | 56.3              | 54.0 | 71.3 | 29.8 | 37.6 | 42.3 | 37.9 |
|                   |                   | 90   | 66.9 |      | 41.9 | 55.6 | 49.7 |
| 321               | 36.7              | 19.1 | 22.2 | 17.0 | 10.9 | 11.5 | 21.6 |
|                   | 57.7              | 40.9 | 51.9 | 33.2 | 29.2 | 27.0 | 32.3 |
|                   |                   | 74.5 | 55.5 | 72.0 | 53.3 | 40.2 | 36.7 |
|                   |                   |      | 90   |      |      |      | 40.5 |
| 331               | 46.5              | 13.1 | 22.0 |      |      |      |      |
| 510               | 11.4              |      |      |      |      |      |      |
| 511               | 15.6              |      |      |      |      |      |      |
| 711               | 11.3              |      |      |      |      |      |      |

Largely from R. M. Bozorth, *Phys. Rev.* **26**, 390 (1925); rounded off to the nearest 0.1°.

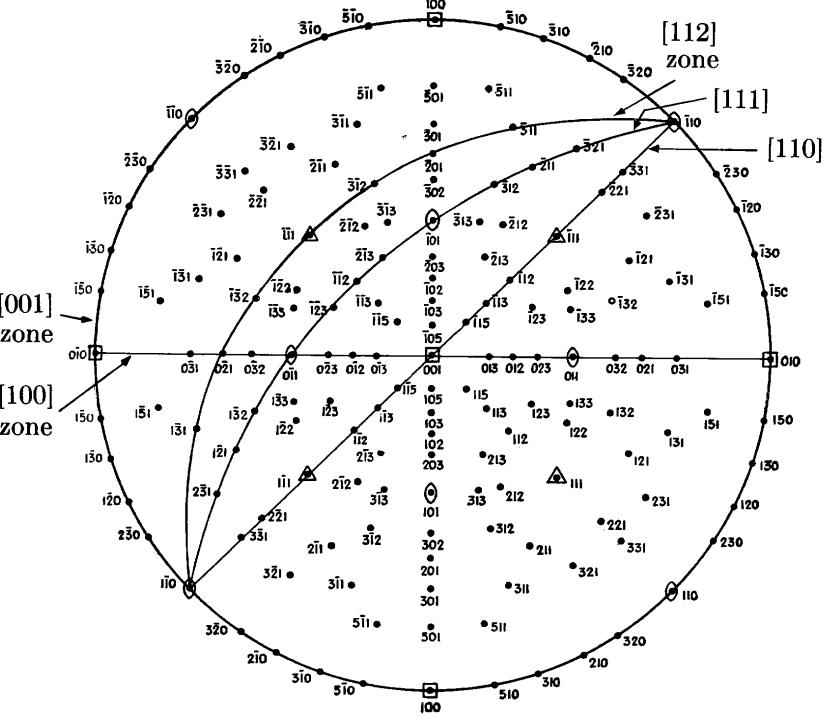


FIG. 2-37. Standard (001) projection of a cubic crystal. (From *Structure of Metals*, by C. S. Barrett, McGraw-Hill Book Company, Inc., 1952.)

this way we locate (011), for example, on the great circle joining (001) and (010) and at 45° from each. After all the {110} poles are plotted, we can find the {111} poles at the intersection of zone circles. Inspection of a crystal model or drawing or use of the zone relation given by Eq. (2-3) will show that (111), for example, belongs to both the zone  $[\bar{1}01]$  and the zone  $[0\bar{1}1]$ . The pole of (111) is thus located at the intersection of the zone circle through (010), (101), and (010) and the zone circle through (100), (011), and (100). This location may be checked by measurement of its angular distance from (010) or (100), which should be 54.7°. The (011) standard projection shown in Fig. 2-36(b) is plotted in the same manner. Alternately, it may be constructed by rotating all the poles in the (001) projection 45° to the left about the NS axis of the projection, since this operation will bring the (011) pole to the center. In both of these projections symmetry symbols have been given each pole in conformity with Fig. 2-6(b), and it will be noted that the projection itself has the symmetry of the axis perpendicular to its plane, Figs. 2-36(a) and (b) having 4-fold and 2-fold symmetry, respectively.

## THE GEOMETRY OF CRYSTALS

[CHAP. 2]

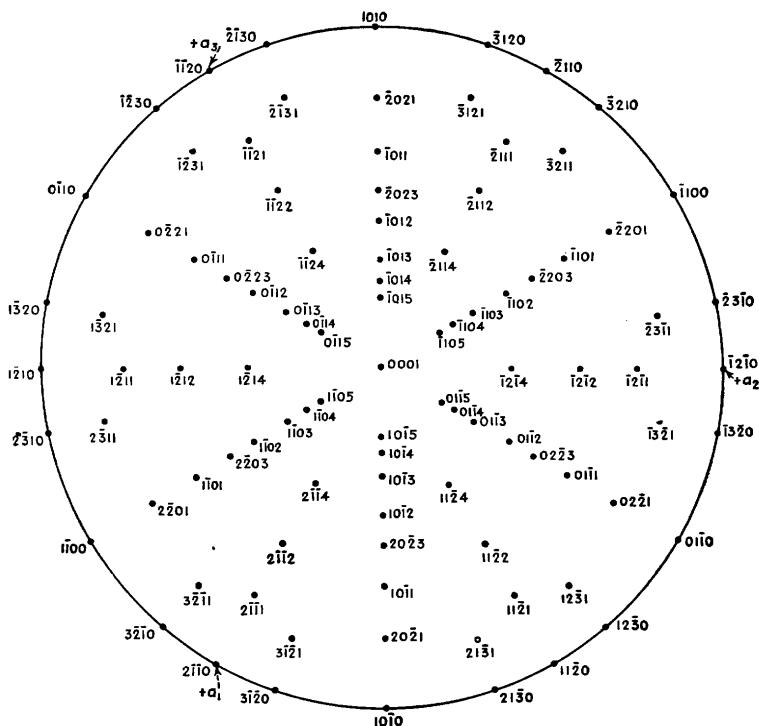


FIG. 2-38. Standard (0001) projection for zinc (hexagonal,  $c/a = 1.86$ ). (From *Structure of Metals*, by C. S. Barrett, McGraw-Hill Book Company, Inc., 1952.)

Figure 2-37 is a standard (001) projection of a cubic crystal with considerably more detail and a few important zones indicated. A standard (0001) projection of a hexagonal crystal (zinc) is given in Fig. 2-38.

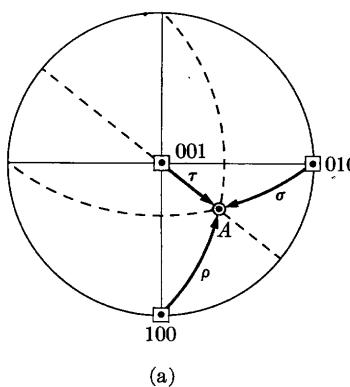
It is sometimes necessary to determine the *Miller indices of a given pole* on a crystal projection, for example the pole  $A$  in Fig. 2-39(a), which applies to a cubic crystal. If a detailed standard projection is available, the projection with the unknown pole can be superimposed on it and its indices will be disclosed by its coincidence with one of the known poles on the standard. Alternatively, the method illustrated in Fig. 2-39 may be used. The pole  $A$  defines a direction in space, normal to the plane  $(hkl)$  whose indices are required, and this direction makes angles  $\rho$ ,  $\sigma$ ,  $\tau$  with the coordinate axes  $a$ ,  $b$ ,  $c$ . These angles are measured on the projection as shown in (a). Let the perpendicular distance between the origin and the  $(hkl)$  plane nearest the origin be  $d$  [Fig. 2-39(b)], and let the direction cosines of the line  $A$  be  $p$ ,  $q$ ,  $r$ . Therefore

$$p = \cos \rho = \frac{d}{a/h}, \quad q = \cos \sigma = \frac{d}{b/k}, \quad r = \cos \tau = \frac{d}{c/l},$$

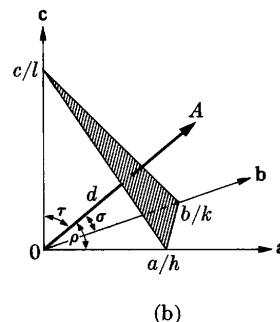
2-11]

## THE STEREOGRAPHIC PROJECTION

75



(a)



(b)

FIG. 2-39. Determination of the Miller indices of a pole.

$$h:k:l = pa:qb:rc. \quad (2-8)$$

For the cubic system we have the simple result that the Miller indices required are in the same ratio as the direction cosines.

The lattice reorientation caused by *twinning* can be clearly shown on the stereographic projection. In Fig. 2-40 the open symbols are the  $\{100\}$  poles of a cubic crystal projected on the  $(001)$  plane. If this crystal is FCC, then one of its possible twin planes is  $(111)$ , represented on the projection both by its pole and its trace. The cube poles of the twin formed by reflection in this plane are shown as solid symbols; these poles are located by rotating the projection on a Wulff net until the pole of the twin plane lies on the equator, after which the cube poles of the crystal can be moved along latitude circles of the net to their final position.

The main principles of the stereographic projection have now been presented, and we will have occasion to use them later in dealing with various practical problems in x-ray metallography. The student is reminded, however, that a mere reading of this section is not sufficient preparation for such problems. In order to gain real familiarity with the stereographic projection, he must practice, with Wulff net and tracing paper, the operations described above and solve problems of the kind given below. Only in this way will he be able to read and manipulate the stereographic projection with facility and think in three dimensions of what is represented in two.

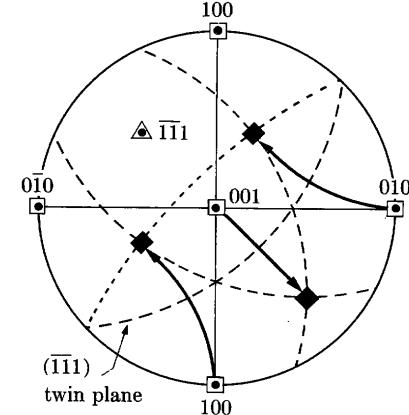


FIG. 2-40. Stereographic projection of an FCC crystal and its twin.

## PROBLEMS

**2-1.** Draw the following planes and directions in a tetragonal unit cell: (001), (011), (113), [110], [201], [101].

**2-2.** Show by means of a (110) sectional drawing that [111] is perpendicular to (111) in the cubic system, but not, in general, in the tetragonal system.

**2-3.** In a drawing of a hexagonal prism, indicate the following planes and directions: (1210), (1012), (1011), [110], [111], [021].

**2-4.** Derive Eq. (2-2) of the text.

**2-5.** Show that the planes (110), (121), and (312) belong to the zone [111].

**2-6.** Do the following planes all belong to the same zone: (110), (311), (132)? If so, what is the zone axis? Give the indices of any other plane belonging to this zone.

**2-7.** Prepare a cross-sectional drawing of an HCP structure which will show that all atoms do not have identical surroundings and therefore do not lie on a point lattice.

**2-8.** Show that  $c/a$  for hexagonal close packing of spheres is 1.633.

**2-9.** Show that the HCP structure (with  $c/a = 1.633$ ) and the FCC structure are equally close-packed, and that the BCC structure is less closely packed than either of the former.

**2-10.** The unit cells of several orthorhombic crystals are described below. What is the Bravais lattice of each and how do you know?

- (a) Two atoms of the same kind per unit cell located at  $0 \frac{1}{2} 0, \frac{1}{2} 0 \frac{1}{2}$ .
- (b) Four atoms of the same kind per unit cell located at  $0 0 z, 0 \frac{1}{2} z, 0 \frac{1}{2} (\frac{1}{2} + z), 0 0 (\frac{1}{2} + z)$ .
- (c) Four atoms of the same kind per unit cell located at  $x y z, \bar{x} \bar{y} z, (\frac{1}{2} + x) (\frac{1}{2} - y) \bar{z}, (\frac{1}{2} - x) (\frac{1}{2} + y) \bar{z}$ .
- (d) Two atoms of one kind A located at  $\frac{1}{2} 0 0, 0 \frac{1}{2} \frac{1}{2}$ ; and two atoms of another kind B located at  $0 0 \frac{1}{2}, \frac{1}{2} \frac{1}{2} 0$ .

**2-11.** Make a drawing, similar to Fig. 2-23, of a (112) twin in a BCC lattice and show the shear responsible for its formation. Obtain the magnitude of the shear strain graphically.

**2-12.** Construct a Wulff net, 18 cm in diameter and graduated at  $30^\circ$  intervals, by the use of compass, dividers, and straightedge only. Show all construction lines.

*In some of the following problems, the coordinates of a point on a stereographic projection are given in terms of its latitude and longitude, measured from the center of the projection. Thus, the N pole is  $90^\circ N, 0^\circ E$ , the E pole is  $0^\circ N, 90^\circ E$ , etc.*

**2-13.** Plane A is represented on a stereographic projection by a great circle passing through the N and S poles and the point  $0^\circ N, 70^\circ W$ . The pole of plane B passing through the N and S poles and the point  $30^\circ N, 50^\circ W$ .

- (a) Find the angle between the two planes.
- (b) Draw the great circle of plane B and demonstrate that the stereographic projection is angle-true by measuring with a protractor the angle between the great circles of A and B.

## PROBLEMS

**2-14.** Pole A, whose coordinates are  $20^\circ N, 50^\circ E$ , is to be rotated about the axes described below. In each case, find the coordinates of the final position of pole A and show the path traced out during its rotation.

- (a)  $100^\circ$  rotation about the NS axis, counterclockwise looking from N to S.
- (b)  $60^\circ$  rotation about an axis normal to the plane of projection, clockwise to the observer.
- (c)  $60^\circ$  rotation about an inclined axis B, whose coordinates are  $10^\circ S, 30^\circ W$ , clockwise to the observer.

**2-15.** Draw a standard (111) projection of a cubic crystal, showing all poles of the form {100}, {110}, {111} and the important zone circles between them. Compare with Figs. 2-36(a) and (b).

**2-16.** Draw a standard (001) projection of white tin (tetragonal,  $c/a = 0.545$ ), showing all poles of the form {001}, {100}, {110}, {011}, {111} and the important zone circles between them. Compare with Fig. 2-36(a).

**2-17.** Draw a standard (0001) projection of beryllium (hexagonal,  $c/a = 1.57$ ), showing all poles of the form {2110}, {1010}, {2111}, {1011} and the important zone circles between them. Compare with Fig. 2-38.

**2-18.** On a standard (001) projection of a cubic crystal, in the orientation of Fig. 2-36(a), the pole of a certain plane has coordinates  $53.3^\circ S, 26.6^\circ E$ . What are its Miller indices? Verify your answer by comparison of measured angles with those given in Table 2-3.

**2-19.** Duplicate the operations shown in Fig. 2-40 and thus find the locations of the cube poles of a (111) reflection twin in a cubic crystal. What are their coordinates?

**2-20.** Show that the twin orientation found in Prob. 2-19 can also be obtained by

- (a) Reflection in a {112} plane. Which one?
- (b)  $180^\circ$  rotation about a  $\langle 111 \rangle$  axis. Which one?
- (c)  $60^\circ$  rotation about a  $\langle 111 \rangle$  axis. Which one?

In (c), show the paths traced out by the cube poles during their rotation.