# 4
# *Crystal Lattices*

Those who have not wandered amidst the mineralogical departments of natural history museums are often surprised to learn that metals, like most other solids, are crystalline, for although one is used to the very obvious crystalline features of quartz, diamond, and rock salt, the characteristic plane faces at sharp angles with one another are absent from metals in their most commonly encountered forms. However, those metals that occur naturally in the metallic state are quite often found in crystalline forms, which are completely disguised in finished metal products by the great malleability of metals, which permits them to be fashioned into whatever macroscopic shape one wishes.

The true test of crystallinity is not the superficial appearance of a large specimen, but whether on the microscopic level the ions are arranged in a periodic array.[1] This underlying microscopic regularity of crystalline matter was long hypothesized as the obvious way to account for the simple geometric regularities of macroscopic crystals, in which plane faces make only certain definite angles with each other. It received direct experimental confirmation in 1913 through the work of W. and L. Bragg, who founded the subject of X-ray crystallography and began the investigation of how atoms are arranged in solids.

Before we describe how the microscopic structure of solids is determined by X-ray diffraction and how the periodic structures so revealed affect fundamental physical properties, it is useful to survey some of the most important geometrical properties of periodic arrays in three-dimensional space. These purely geometrical considerations are implicit in almost all the analysis one encounters throughout solid state physics, and shall be pursued in this chapter and in Chapters 5 and 7. The first of many applications of these concepts will be made to X-ray diffraction in Chapter 6.

## BRAVAIS LATTICE

A fundamental concept in the description of any crystalline solid is that of the *Bravais lattice*, which specifies the periodic array in which the repeated units of the crystal are arranged. The units themselves may be single atoms, groups of atoms, molecules, ions, etc., but the Bravais lattice summarizes only the geometry of the underlying periodic structure, regardless of what the actual units may be. We give two equivalent definitions of a Bravais lattice[2]:

(a)   A Bravais lattice is an infinite array of discrete points with an arrangement and orientation that appears *exactly* the same, from whichever of the points the array is viewed.

(b)   A (three-dimensional) Bravais lattice consists of all points with position vectors **R** of the form

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3, \tag{4.1}$$

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[1]   Often a specimen is made up of many small pieces, each large on the microscopic scale and containing large numbers of periodically arranged ions. This "polycrystalline" state is more commonly encountered than a single macroscopic crystal, in which the periodicity is perfect, extending through the entire specimen.

[2]   Why the name Bravais appears is explained in Chapter 7.

where $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ are any three vectors not all in the same plane, and $n_1$, $n_2$, and $n_3$ range through all integral values.[3] Thus the point $\Sigma n_i \mathbf{a}_i$ is reached by moving $n_i$ steps[4] of length $a_i$ in the direction of $\mathbf{a}_i$ for $i = 1, 2,$ and $3$.

The vectors $\mathbf{a}_i$ appearing in definition (b) of a Bravais lattice are called *primitive vectors* and are said to *generate* or *span* the lattice.

It takes some thought to see that the two definitions of a Bravais lattice are equivalent. That any array satisfying (b) also satisfies (a) becomes evident as soon as both definitions are understood. The argument that *any* array satisfying definition (a) can be generated by an appropriate set of three vectors is not as obvious. The proof consists of an explicit recipe for constructing three primitive vectors. The construction is given in Problem 8a.
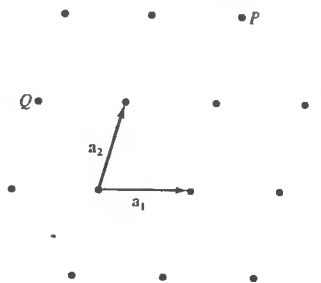


**Figure 4.1**

A general two-dimensional Bravais lattice of no particular symmetry: the oblique net. Primitive vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ are shown. All points in the net are linear combinations of these with integral coefficients; for example, $P = \mathbf{a}_1 + 2\mathbf{a}_2$, and $Q = -\mathbf{a}_1 + \mathbf{a}_2$.

Figure 4.1 shows a portion of a two-dimensional Bravais lattice.[5] Clearly definition (a) is satisfied, and the primitive vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ required by definition (b) are indicated in the figure. Figure 4.2 shows one of the most familiar of three-dimensional Bravais lattices, the simple cubic. It owes its special structure to the fact that it can be spanned by three mutually perpendicular primitive vectors of equal length.
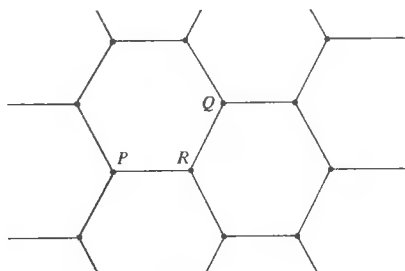
**Figure 4.2**

A simple cubic three-dimensional Bravais lattice. The three primitive vectors can be taken to be mutually perpendicular, and with a common magnitude.



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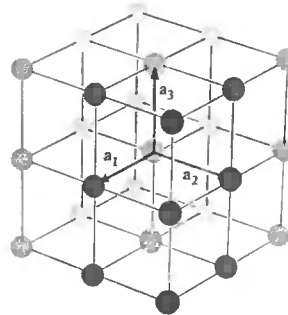
[3]    We continue with the convention that "integer" means a negative integer or zero, as well as a positive integer.

[4]    When $n$ is negative, $n$ steps in a direction means $n$ steps in the opposite direction. The point reached does not, of course, depend on the order in which the $n_1 + n_2 + n_3$ steps are taken.

[5]    A two-dimensional Bravais lattice is also known as a *net.*

**Figure 4.3**
The vertices of a two-dimensional honeycomb do *not* form a Bravais lattice. The array of points has the same appearance whether viewed from point $P$ or point $Q$. However, the view from point $R$ is rotated through 180°.

It is important that not only the arrangement, but also the orientation must appear the same from every point in a Bravais lattice. Consider the vertices of a two-dimensional honeycomb (Figure 4.3). The array of points looks the same when viewed from adjacent points only if the page is rotated through 180° each time one moves from one point to the next. Structural relations are clearly identical, but *not* orientational relations, so the vertices of a honeycomb do not form a Bravais lattice. A case of more practical interest, satisfying the structural but not the orientational requirements of definition (a), is the three-dimensional hexagonal close-packed lattice, described below.

## INFINITE LATTICES AND FINITE CRYSTALS

Since all points are equivalent, the Bravais lattice must be infinite in extent. Actual crystals are, of course, finite, but if they are large enough the vast majority of points will be so far from the surface as to be unaffected by its existence. The fiction of an infinite system is thus a very useful idealization. If surface effects are of interest the notion of a Bravais lattice is still relevant, but now one must think of the physical crystal as filling up only a finite portion of the ideal Bravais lattice.

Frequently one considers finite crystals, not because surface effects are important, but simply for conceptual convenience, just as in Chapter 2 we placed the electron gas in a cubical box of volume $V = L^3$. One then generally picks the finite region of the Bravais lattice to have the simplest possible form. Given three primitive vectors $a_1$, $a_2$, and $a_3$, one usually considers the finite lattice of $N$ sites to be the set of points of the form $R = n_1 a_1 + n_2 a_2 + n_3 a_3$, where $0 \leqslant n_1 < N_1, 0 \leqslant n_2 < N_2$, $0 \leqslant n_3 < N_3$, and $N = N_1 N_2 N_3$. This artifact is closely connected with the generalization to the description of crystalline systems[6] of the periodic boundary condition we used in Chapter 2.

## FURTHER ILLUSTRATIONS AND IMPORTANT EXAMPLES

Of the two definitions of a Bravais lattice, definition (b) is mathematically more precise and is the obvious starting point for any analytic work. It has, however, two

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[6]    We shall make particular use of it in Chapters 8 and 22.

minor shortcomings. First, for any given Bravais lattice the set of primitive vectors is not unique—indeed, there are infinitely many nonequivalent choices (see Figure 4.4)—and it is distasteful (and sometimes misleading) to rely too heavily on a definition that emphasizes a particular choice. Second, when presented with a particular array of points one usually can tell at a glance whether the first definition is satisfied, although the existence of a set of primitive vectors or a proof that there is no such set can be rather more difficult to perceive immediately.
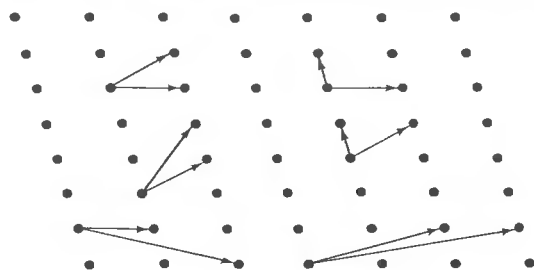


**Figure 4.4**
Several possible choices of pairs of primitive vectors for a two-dimensional Bravais lattice. They are drawn, for clarity, from different origins.

Consider, for example, the *body-centered cubic* (bcc) lattice, formed by adding to the simple cubic lattice of Figure 4.2 (whose sites we now label $A$) an additional point, $B$, at the center of each little cube (Figure 4.5). One might at first feel that the center points $B$ bear a different relation to the whole than the corner points $A$. However, the center point $B$ can be thought of as corner points of a second simple cubic array.

**Figure 4.5**
A few sites from a body-centered cubic Bravais lattice. Note that it can be regarded either as a simple cubic lattice formed from the points $A$ with the points $B$ at the cube centers, or as a simple cubic lattice formed from the points $B$ with the points $A$ at the cube centers. This observation establishes that it is indeed a Bravais lattice.
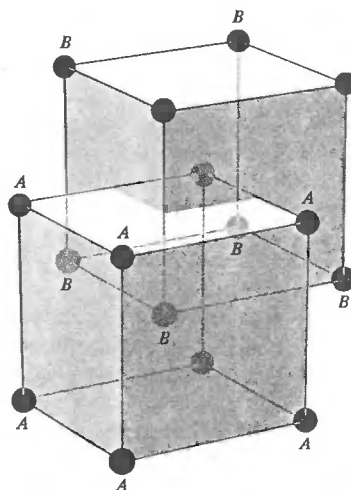


In this new array the corner points $A$ of the original cubic array are center points. Thus all points do have identical surroundings, and the body-centered cubic lattice is a Bravais lattice. If the original simple cubic lattice is generated by primitive vectors

$$a\hat{x}, \quad a\hat{y}, \quad a\hat{z}, \tag{4.2}$$

where $\hat{x}$, $\hat{y}$, and $\hat{z}$ are three orthogonal unit vectors, then a set of primitive vectors for the body-centered cubic lattice could be (Figure 4.6)

$$\mathbf{a}_1 = a\hat{x}, \quad \mathbf{a}_2 = a\hat{y}, \quad \mathbf{a}_3 = \frac{a}{2}(\hat{x} + \hat{y} + \hat{z}). \tag{4.3}$$
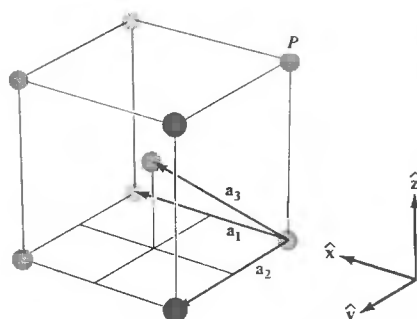


**Figure 4.6**
Three primitive vectors, specified in Eq. (4.3), for the body-centered cubic Bravais lattice. The lattice is formed by taking all linear combinations of the primitive vectors with integral coefficients. The point $P$, for example, is $P = -\mathbf{a}_1 - \mathbf{a}_2 + 2\mathbf{a}_3$.

A more symmetric set (see Figure 4.7) is

$$\mathbf{a}_1 = \frac{a}{2}(\hat{y} + \hat{z} - \hat{x}), \quad \mathbf{a}_2 = \frac{a}{2}(\hat{z} + \hat{x} - \hat{y}), \quad \mathbf{a}_3 = \frac{a}{2}(\hat{x} + \hat{y} - \hat{z}). \tag{4.4}$$

It is important to convince oneself both geometrically and analytically that these sets do indeed generate the bcc Bravais lattice.
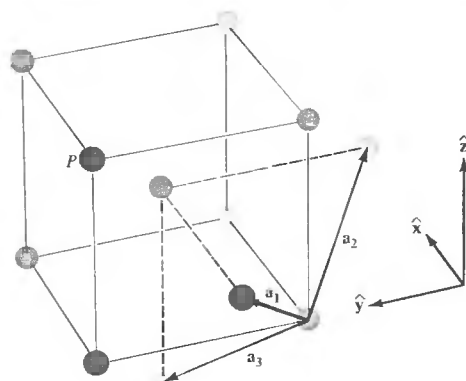


**Figure 4.7**
A more symmetric set of primitive vectors, specified in Eq. (4.4), for the body-centered cubic Bravais lattice. The point $P$, for example, has the form $P = 2\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3$.

Another equally important example is the *face-centered cubic* (fcc) Bravais lattice. To construct the face-centered cubic Bravais lattice add to the simple cubic lattice of Figure 4.2 an additional point in the center of each square face (Figure 4.8). For ease in description think of each cube in the simple cubic lattice as having horizontal bottom and top faces, and four vertical side faces facing north, south, east, and west. It may sound as if all points in this new array are not equivalent, but in fact they are. One can, for example, consider the *new* simple cubic lattice formed by the points added

**Figure 4.8**
Some points from a face-centered cubic Bravais lattice.
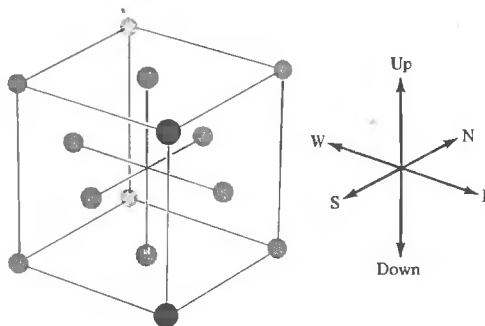
to the centers of all the horizontal faces. The original simple cubic lattice points are now centering points on the horizontal faces of the new simple cubic lattice, whereas the points that were added to the centers of the north-south faces of the original cubic lattice are in the centers of the east-west faces of the new one, and vice versa.

In the same way one can also regard the simple cubic lattice as being composed of all points centering the north-south faces of the original simple cubic lattice, or all points centering the east-west faces of the original cubic lattice. In either case the remaining points will be found centered on the faces of the new simple cubic framework. Thus any point can be thought of either as a corner point or as a face-centering point for any of the three kinds of faces, and the face-centered cubic lattice is indeed a Bravais lattice.

A symmetric set of primitive vectors for the face-centered cubic lattice (see Figure 4.9) is

$$\mathbf{a}_1 = \frac{a}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}}), \quad \mathbf{a}_2 = \frac{a}{2}(\hat{\mathbf{z}} + \hat{\mathbf{x}}), \quad \mathbf{a}_3 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}}). \tag{4.5}$$

**Figure 4.9**
A set of primitive vectors, as given in Eq. (4.5), for the face-centered cubic Bravais lattice. The labeled points are $P = \mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3$, $Q = 2\mathbf{a}_2$, $R = \mathbf{a}_2 + \mathbf{a}_3$, and $S = -\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3$.
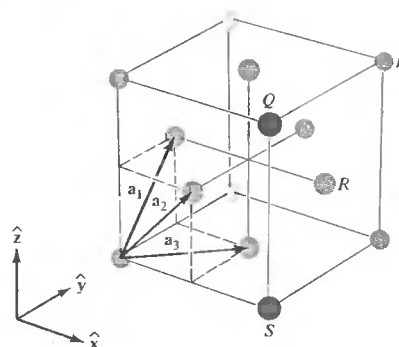
The face-centered cubic and body-centered cubic Bravais lattices are of great importance, since an enormous variety of solids crystallize in these forms with an atom (or ion) at each lattice site (see Tables 4.1 and 4.2). (The corresponding simple cubic form, however, is very rare, the alpha phase of polonium being the only known example among the elements under normal conditions.)

Table 4.1
**ELEMENTS WITH THE MONATOMIC FACE-CENTERED
CUBIC CRYSTAL STRUCTURE**

| ELEMENT | $a$ (Å) | ELEMENT | $a$ (Å) | ELEMENT | $a$ (Å) |
|---|---|---|---|---|---|
| Ar | 5.26 (4.2 K) | Ir | 3.84 | Pt | 3.92 |
| Ag | 4.09 | Kr | 5.72 (58 K) | $\delta$-Pu | 4.64 |
| Al | 4.05 | La | 5.30 | Rh | 3.80 |
| Au | 4.08 | Ne | 4.43 (4.2 K) | Sc | 4.54 |
| Ca | 5.58 | Ni | 3.52 | Sr | 6.08 |
| Ce | 5.16 | Pb | 4.95 | Th | 5.08 |
| $\beta$-Co | 3.55 | Pd | 3.89 | Xe (58 K) | 6.20 |
| Cu | 3.61 | Pr | 5.16 | Yb | 5.49 |

Data in Tables 4.1 to 4.7 are from R. W. G. Wyckoff, *Crystal Structures*, 2nd ed., Interscience, New York, 1963. In most cases, the data are taken at about room temperature and normal atmospheric pressure. For elements that exist in many forms the stable room temperature form (or forms) is given. For more detailed information, more precise lattice constants, and references, the Wyckoff work should be consulted.

Table 4.2
**ELEMENTS WITH THE MONATOMIC BODY-CENTERED
CUBIC CRYSTAL STRUCTURE**

| ELEMENT | $a$ (Å) | ELEMENT | $a$ (Å) | ELEMENT | $a$ (Å) |
|---|---|---|---|---|---|
| Ba | 5.02 | Li | 3.49 (78 K) | Ta | 3.31 |
| Cr | 2.88 | Mo | 3.15 | Tl | 3.88 |
| Cs | 6.05 (78 K) | Na | 4.23 (5 K) | V | 3.02 |
| Fe | 2.87 | Nb | 3.30 | W | 3.16 |
| K | 5.23 (5 K) | Rb | 5.59 (5 K) | | |

## A NOTE ON USAGE

Although we have defined the term "Bravais lattice" to apply to a set of points, it is also generally used to refer to the set of vectors joining any one of these points to all the others. (Because the points *are* a Bravais lattice, this set of vectors does not depend on which point is singled out as the origin.) Yet another usage comes from the fact that any vector **R** determines a *translation* or *displacement*, in which everything is moved bodily through space by a distance $R$ in the direction of **R**. The term "Bravais lattice" is also used to refer to the set of translations determined by the vectors, rather than the vectors themselves. In practice it is always clear from the context whether it is the points, the vectors, or the translations that are being referred to.[7]

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[7] The more general use of the term provides an elegant definition of a Bravais lattice with the precision of definition (b) and the nonprejudicial nature of definition (a): A Bravais lattice is a discrete set of vectors not all in a plane, closed under vector addition and subtraction (i.e., the sum and difference of any two vectors in the set are also in the set).

## COORDINATION NUMBER

The points in a Bravais lattice that are closest to a given point are called its *nearest neighbors*. Because of the periodic nature of a Bravais lattice, each point has the same number of nearest neighbors. This number is thus a property of the lattice, and is referred to as the *coordination number* of the lattice. A simple cubic lattice has co-ordination number 6; a body-centered cubic lattice, 8; and a face-centered cubic lattice, 12. The notion of a coordination number can be extended in the obvious way to some simple arrays of points that are not Bravais lattices, provided that each point in the array has the same number of nearest neighbors.

## PRIMITIVE UNIT CELL

A volume of space that, when translated through all the vectors in a Bravais lattice, just fills all of space without either overlapping itself or leaving voids is called a *primitive cell* or *primitive unit cell* of the lattice.[8] There is no unique way of choosing a primitive cell for a given Bravais lattice. Several possible choices of primitive cells for a two-dimensional Bravais lattice are illustrated in Figure 4.10.
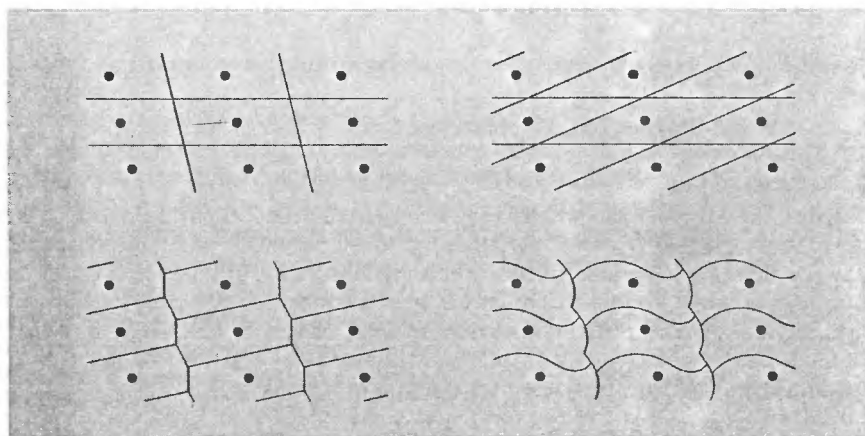


**Figure 4.10**
Several possible choices of primitive cell for a single two-dimensional Bravais lattice.

A primitive cell must contain precisely one lattice point (unless it is so positioned that there are points on its surface). It follows that if $n$ is the density of points in the lattice[9] and $v$ is the volume of the primitive cell, then $nv = 1$. Thus $v = 1/n$. Since

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[8]   Translations of the primitive cell may possess common surface points; the nonoverlapping proviso is only intended to prohibit overlapping regions of nonzero volume.

[9]   The density $n$ of Bravais lattice points need not, of course, be identical to the density of conduction electrons in a metal. When the possibility of confusion is present, we shall specify the two densities with different symb°¹⁻

this result holds for any primitive cell, the volume of a primitive cell is independent of the choice of cell.

It also follows from the definition of a primitive cell that, given any two primitive cells of arbitrary shape, it is possible to cut the first up into pieces, which, when translated through appropriate lattice vectors, can be reassembled to give the second. This is illustrated in Figure 4.11.
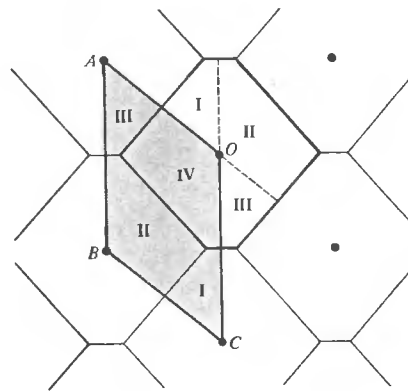


**Figure 4.11**
Two possible primitive cells for a two-dimensional Bravais lattice. The parallelogram cell (shaded) is obviously primitive; additional hexagonal cells are indicated to demonstrate that the hexagonal cell is also primitive. The parallelogram can be cut into pieces, which, when translated through lattice vectors, reassemble to form the hexagon. The translations for the four regions of the parallelogram are: Region I—$\overrightarrow{CO}$; Region II—$\overrightarrow{BO}$; Region III—$\overrightarrow{AO}$; Region IV—no translation.

The obvious primitive cell to associate with a particular set of primitive vectors, $a_1, a_2, a_3$, is the set of all points $r$ of the form

$$r = x_1 a_1 + x_2 a_2 + x_3 a_3 \tag{4.6}$$

for all $x_i$ ranging continuously between 0 and 1; i.e., the parallelipiped spanned by the three vectors $a_1, a_2$, and $a_3$. This choice has the disadvantage of not displaying the full symmetry of the Bravais lattice. For example (Figure 4.12), the unit cell (4.6) for the choice of primitive vectors (4.5) of the fcc Bravais lattice is an oblique parallelipiped, which does not have the full cubic symmetry of the lattice in which it is embedded. It is often important to work with cells that do have the full symmetry of their Bravais lattice. There are two widely used solutions to this problem:
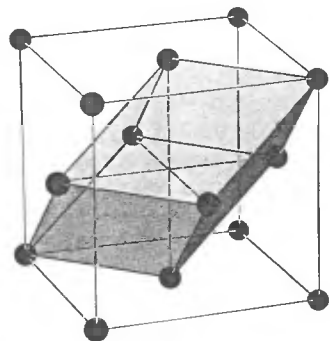


**Figure 4.12**
Primitive and conventional unit cells for the face-centered cubic Bravais lattice. The conventional cell is the large cube. The primitive cell is the figure with six parallelogram faces. It has one quarter the volume of the cube, and rather less symmetry.

## UNIT CELL; CONVENTIONAL UNIT CELL

One can fill space up with nonprimitive unit cells (known simply as *unit cells* or *conventional unit cells*). A unit cell is a region that just fills space without any overlapping when translated through some *subset* of the vectors of a Bravais lattice. The conventional unit cell is generally chosen to be bigger than the primitive cell and to have the required symmetry. Thus one frequently describes the body-centered cubic lattice in terms of a cubic unit cell (Figure 4.13) that is twice as large as a primitive bcc unit cell, and the face-centered cubic lattice in terms of a cubic unit cell (Figure 4.12) that has four times the volume of a primitive fcc unit cell. (That the conventional cells are two and four times bigger than the primitive cells is easily seen by asking how many lattice points the conventional cubic cell must contain when it is so placed that no points are on its surface.) Numbers specifying the size of a unit cell (such as the single number $a$ in cubic crystals) are called *lattice constants*.

**Figure 4.13**
Primitive and conventional unit cells for the body-centered cubic Bravais lattice. The primitive cell (shaded) has half the volume of the conventional cubic cell.
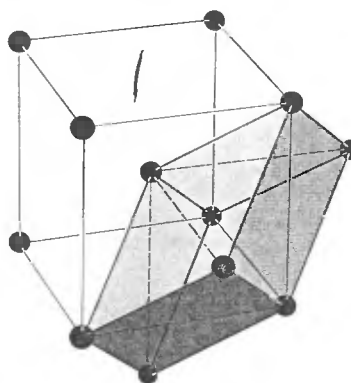


## WIGNER-SEITZ PRIMITIVE CELL

One can always choose a *primitive* cell with the full symmetry of the Bravais lattice. By far the most common such choice is the *Wigner-Seitz cell*. The Wigner-Seitz cell about a lattice point is the region of space that is closer to that point than to any other lattice point.[10] Because of the translational symmetry of the Bravais lattice, the Wigner-Seitz cell about any one lattice point must be taken into the Wigner-Seitz cell about any other, when translated through the lattice vector that joins the two points. Since any point in space has a unique lattice point, as its nearest neighbor[11] it will belong to the Wigner-Seitz cell of precisely one lattice point. It follows that a

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[10]  Such a cell can be defined for any set of discrete points that do not necessarily form a Bravais lattice. In this broader context the cell is known as a Voronoy polyhedron. In contrast to the Wigner-Seitz cell, the structure and orientation of a general Voronoy polyhedron will depend on which point of the array it encloses.

[11]  Except for points on the common surface of two or more Wigner-Seitz cells.

Wigner-Seitz cell, when translated through all lattice vectors, will just fill space without overlapping; i.e., the Wigner-Seitz cell is a primitive cell.

Since there is nothing in the definition of the Wigner-Seitz cell that refers to any particular choice of primitive vectors, the Wigner-Seitz cell will be as symmetrical as the Bravais lattice.[12]

The Wigner-Seitz unit cell is illustrated for a two-dimensional Bravais lattice in Figure 4.14 and for the three-dimensional body-centered cubic and face-centered cubic Bravais lattices in Figures 4.15 and 4.16.

Note that the Wigner-Seitz unit cell about a lattice point can be constructed by drawing lines connecting the point to all others[13] in the lattice, bisecting each line
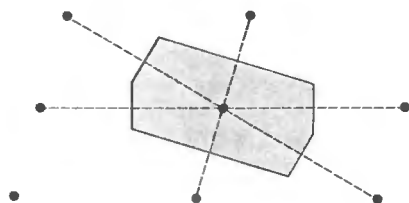


**Figure 4.14**
The Wigner-Seitz cell for a two-dimensional Bravais lattice. The six sides of the cell bisect the lines joining the central points to its six nearest neighboring points (shown as dashed lines). In two dimensions the Wigner-Seitz cell is always a hexagon unless the lattice is rectangular (see Problem 4a).

**Figure 4.15**
The Wigner-Seitz cell for the body-centered cubic Bravais lattice (a "truncated octahedron"). The surrounding cube is a conventional body-centered cubic cell with a lattice point at its center and on each vertex. The hexagonal faces bisect the lines joining the central point to the points on the vertices (drawn as solid lines). The square faces bisect the lines joining the central point to the central points in each of the six neighboring cubic cells (not drawn). The hexagons are regular (see Problem 4d).
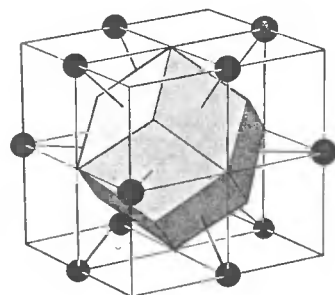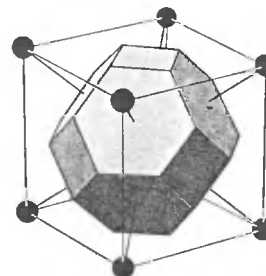




**Figure 4.16**
Wigner-Seitz cell for the face-centered cubic Bravais lattice (a "rhombic dodecahedron"). The surrounding cube is *not* the conventional cubic cell of Figure 4.12, but one in which lattice points are at the center of the cube and at the center of the 12 edges. Each of the 12 (congruent) faces is perpendicular to a line joining the central point to a point on the center of an edge.

[12]    A precise definition of "as symmetrical as" is given in Chapter 7.
[13]    In practice only a fairly small number of nearby points actually yⁱ    ⁿlanes that bound the cell.

with a plane, and taking the smallest polyhedron containing the point bounded by these planes.

## CRYSTAL STRUCTURE; LATTICE WITH A BASIS

A physical crystal can be described by giving its underlying Bravais lattice, together with a description of the arrangement of atoms, molecules, ions, etc., within a particular primitive cell. When emphasizing the difference between the abstract pattern of points composing the Bravais lattice and an actual physical crystal[14] embodying the lattice, the technical term "crystal structure" is used. A *crystal structure* consists of identical copies of the same physical unit, called the *basis*, located at all the points of a Bravais lattice (or, equivalently, translated through all the vectors of a Bravais lattice). Sometimes the term *lattice with a basis* is used instead. However, "lattice with a basis" is also used in a more general sense to refer to what results even when the basic unit is *not* a physical object or objects, but another set of points. For example, the vertices of a two-dimensional honeycomb, though not a Bravais lattice, can be represented as a two-dimensional triangular Bravais lattice[15] with a two-point basis (Figure 4.17). A crystal structure with a basis consisting of a single atom or ion is often called a monatomic Bravais lattice.
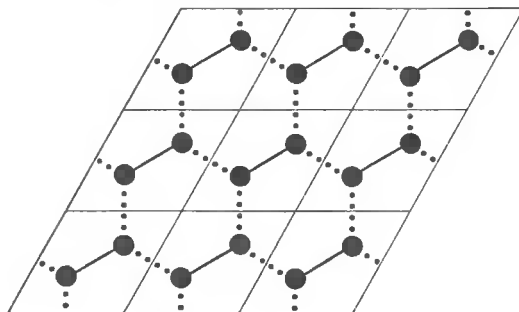


**Figure 4.17**
The honeycomb net, drawn so as to emphasize that it is a Bravais lattice with a two-point basis. The pairs of points joined by heavy solid lines are identically placed in the primitive cells (parallelograms) of the underlying Bravais lattice.

One also can describe a Bravais lattice as a lattice with a basis by choosing a non-primitive conventional unit cell. This is often done to emphasize the cubic symmetry of the bcc and fcc Bravais lattices, which are then described respectively, as simple cubic lattices spanned by $a\hat{x}$, $a\hat{y}$, and $a\hat{z}$, with a two-point basis

$$0, \quad \frac{a}{2}(\hat{x} + \hat{y} + \hat{z}) \qquad \text{(bcc)} \qquad (4.7)$$

or a four-point basis

$$0, \quad \frac{a}{2}(\hat{x} + \hat{y}), \quad \frac{a}{2}(\hat{y} + \hat{z}), \quad \frac{a}{2}(\hat{z} + \hat{x}) \qquad \text{(fcc)}. \qquad (4.8)$$

---

[14] But still idealized in being infinite in extent.

[15] Spanned by two primitive vectors of equal length, making an angle of 60°.

## SOME IMPORTANT EXAMPLES OF CRYSTAL STRUCTURES AND LATTICES WITH BASES

### Diamond Structure

The diamond lattice[16] (formed by the carbon atoms in a diamond crystal) consists of two interpenetrating face-centered cubic Bravais lattices, displaced along the body diagonal of the cubic cell by one quarter the length of the diagonal. It can be regarded as a face-centered cubic lattice with the two-point basis $0$ and $(a/4)(\hat{x} + \hat{y} + \hat{z})$. The coordination number is 4 (Figure 4.18). The diamond lattice is not a Bravais lattice,
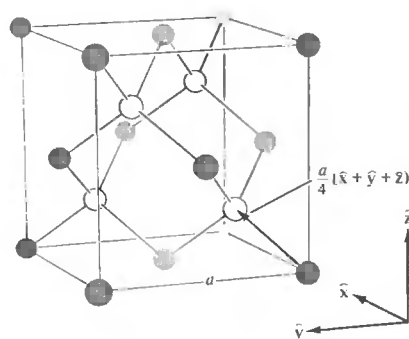


**Figure 4.18**
Conventional cubic cell of the diamond lattice. For clarity, sites corresponding to one of the two interpenetrating face-centered cubic lattices are unshaded. (In the zincblende structure the shaded sites are occupied by one kind of ion, and the unshaded by another.) Nearest-neighbor bonds have been drawn in. The four nearest neighbors of each point form the vertices of a regular tetrahedron.

because the environment of any point differs in orientation from the environments of its nearest neighbors. Elements crystallizing in the diamond structure are given in Table 4.3.

Table 4.3
**ELEMENTS WITH THE DIAMOND CRYSTAL STRUCTURE**

| ELEMENT | CUBE SIDE $a$ (Å) |
|---|---|
| C (diamond) | 3.57 |
| Si | 5.43 |
| Ge | 5.66 |
| $\alpha$-Sn (grey) | 6.49 |

### Hexagonal Close-Packed Structure

Though not a Bravais lattice, the *hexagonal close-packed* (hcp) structure ranks in importance with the body-centered cubic and face-centered cubic Bravais lattices; about 30 elements crystallize in the hexagonal close-packed form (Table 4.4).

---

[16] We use the word "lattice," without qualifications, to refer either to a Bravais lattice or a lattice with a basis.

Table 4.4
**ELEMENTS WITH THE HEXAGONAL CLOSE-PACKED CRYSTAL STRUCTURE**

| ELEMENT | $a$ (Å) | $c$ | $c/a$ | ELEMENT | $a$ (Å) | $c$ | $c/a$ |
|---------|---------|-----|-------|---------|---------|-----|-------|
| Be | 2.29 | 3.58 | 1.56 | Os | 2.74 | 4.32 | 1.58 |
| Cd | 2.98 | 5.62 | 1.89 | Pr | 3.67 | 5.92 | 1.61 |
| Ce | 3.65 | 5.96 | 1.63 | Re | 2.76 | 4.46 | 1.62 |
| α-Co | 2.51 | 4.07 | 1.62 | Ru | 2.70 | 4.28 | 1.59 |
| Dy | 3.59 | 5.65 | 1.57 | Sc | 3.31 | 5.27 | 1.59 |
| Er | 3.56 | 5.59 | 1.57 | Tb | 3.60 | 5.69 | 1.58 |
| Gd | 3.64 | 5.78 | 1.59 | Ti | 2.95 | 4.69 | 1.59 |
| He (2 K) | 3.57 | 5.83 | 1.63 | Tl | 3.46 | 5.53 | 1.60 |
| Hf | 3.20 | 5.06 | 1.58 | Tm | 3.54 | 5.55 | 1.57 |
| Ho | 3.58 | 5.62 | 1.57 | Y | 3.65 | 5.73 | 1.57 |
| La | 3.75 | 6.07 | 1.62 | Zn | 2.66 | 4.95 | 1.86 |
| Lu | 3.50 | 5.55 | 1.59 | Zr | 3.23 | 5.15 | 1.59 |
| Mg | 3.21 | 5.21 | 1.62 | | — | — | |
| Nd | 3.66 | 5.90 | 1.61 | "Ideal" | | | 1.63 |

Underlying the hcp structure is a *simple hexagonal* Bravais lattice, given by stacking two-dimensional triangular nets[15] directly above each other (Figure 4.19). The direction of stacking ($\mathbf{a}_3$, below) is known as the $c$-axis. Three primitive vectors are

$$\mathbf{a}_1 = a\hat{\mathbf{x}}, \quad \mathbf{a}_2 = \frac{a}{2}\hat{\mathbf{x}} + \frac{\sqrt{3}a}{2}\hat{\mathbf{y}}, \quad \mathbf{a}_3 = c\hat{\mathbf{z}}. \tag{4.9}$$

The first two generate a triangular lattice in the $x$-$y$ plane, and the third stacks the planes a distance $c$ above one another.

The hexagonal close-packed structure consists of two interpenetrating simple hexagonal Bravais lattices, displaced from one another by $\mathbf{a}_1/3 + \mathbf{a}_2/3 + \mathbf{a}_3/2$ (Figure 4.20). The name reflects the fact that close-packed hard spheres can be arranged in
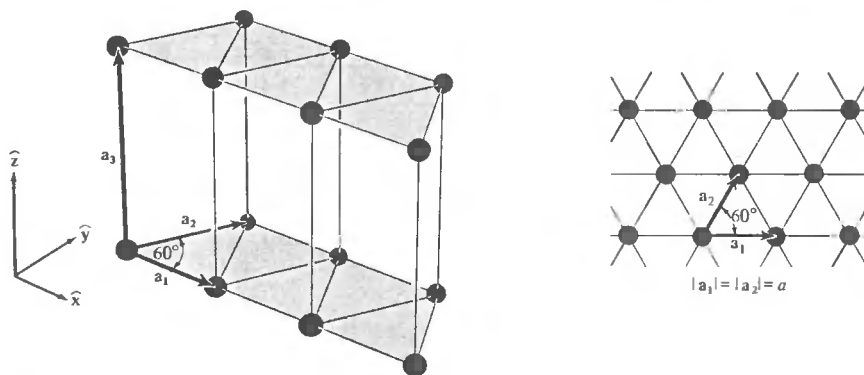


**Figure 4.19**
The simple hexagonal Bravais lattice. Two-dimensional triangular nets (shown in inset) are stacked directly above one another, a distance $c$ apart.
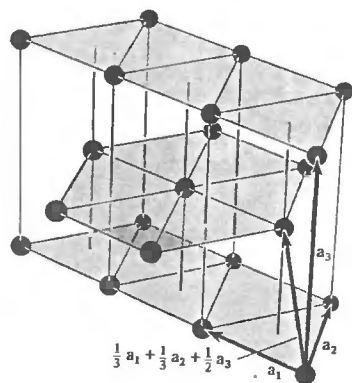
**Figure 4.20**

The hexagonal close-packed crystal structure. It can be viewed as two interpenetrating simple hexagonal Bravais lattices, displaced vertically by a distance $c/2$ along the common $c$-axis, and displaced horizontally so that the points of one lie directly above the centers of the triangles formed by the points of the other.

$\frac{1}{3}\,a_1 + \frac{1}{3}\,a_2 + \frac{1}{2}\,a_3$

such a structure. Consider stacking cannonballs (Figure 4.21), starting with a close-packed triangular lattice as the first layer. The next layer is formed by placing a ball in the depressions left in the center of every other triangle in the first layer, thereby forming a second triangular layer, shifted with respect to the first. The third layer is formed by placing balls in alternate depressions in the second layer, so that they lie directly over the balls in the first layer. The fourth layer lies directly over the second, and so on. The resulting lattice is hexagonal close-packed with the particular value (see Problem 5):

$$c = \sqrt{\frac{8}{3}}\,a = 1.63299a. \tag{4.10}$$

**Figure 4.21**

View from above of the first two layers in a stack of cannonballs. The first layer is arranged in a plane triangular lattice. Balls in the second layer are placed above alternate interstices in the first. If balls in the third layer are placed directly above those in the first, at sites of the type shown in inset (a), balls in the fourth directly above those in the second, etc., the resulting structure will be close-packed hexagonal. If, however, balls in the third layer are placed directly above those interstices in the first that were *not* covered by balls in the second, at sites of the type shown in inset (b), balls in the fourth layer placed directly above those in the first, balls in the fifth directly above those in the second, etc., the resulting structure will be face-centered cubic (with the body diagonal of the cube oriented vertically.)
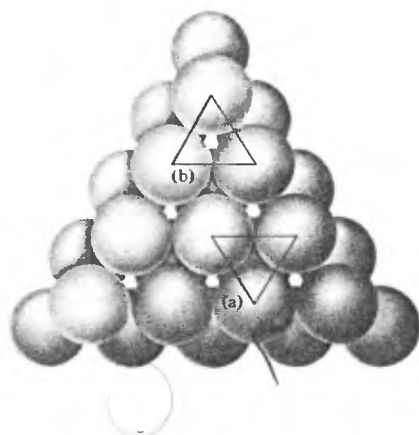
Because, however, the symmetry of the hexagonal close-packed lattice is independent of the $c/a$ ratio, the name is not restricted to this case. The value $c/a = \sqrt{8/3}$ is sometimes called "ideal," and the truly close-packed structure, with the ideal value of $c/a$, is known as an ideal hcp structure. Unless, however, the physical units in the hcp structure are actually close-packed spheres, there is no  son why $c/a$ should be ideal (see Table 4.4).

Note, as in the case of the diamond structure, that the hcp lattice is not a Bravais lattice, because the orientation of the environment of a point varies from layer to layer along the $c$-axis. Note also that, when viewed along the $c$-axis, the two types of planes merge to form the two-dimensional honeycomb array of Figure 4.3, which is not a Bravais lattice.

## Other Close-Packing Possibilities

Note that the hcp structure is not the only way to close-pack spheres. If the first two layers are laid down as described above, but the third is placed in the *other* set of depressions in the second—i.e., those lying above unused depressions in *both* the first and second layers (see Figure 4.21)—and then the fourth layer is placed in depressions in the third directly above the balls in the first, the fifth above the second, and so on, one generates a Bravais lattice. This Bravais lattice turns out to be nothing but the face-centered cubic lattice, with the cube diagonal perpendicular to the triangular planes (Figures 4.22 and 4.23).
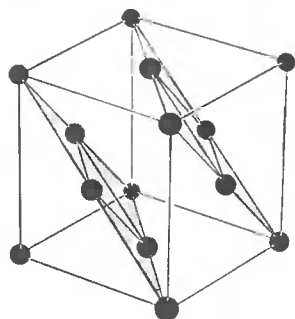


**Figure 4.22**
How to section the face-centered cubic Bravais lattice to get the layers pictured in Figure 4.21.

**Figure 4.23**
A cubic section of some face-centered cubic close-packed spheres.
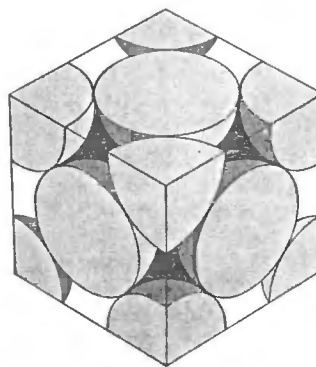


There are infinitely many other close-packing arrangements, since each successive layer can be placed in either of two positions. Only fcc close-packing gives a Bravais lattice, and the fcc (...*ABCABCABC*...) and hcp (...*ABABAB*...) structures are by far the most commonly encountered. Other close-packed structures are observed, however.     ..ain rare earth metals, for example, take on a structure of the form (...*ABACABACABAC*...).

## The Sodium Chloride Structure

We are forced to describe the hexagonal close-packed and diamond lattices as lattices with bases by the intrinsic geometrical arrangement of the lattice points. A lattice with a basis is also necessary, however, in describing crystal structures in which the atoms or ions are located only at the points of a Bravais lattice, but in which the crystal structure nevertheless lacks the full translational symmetry of the Bravais lattice because more than one kind of atom or ion is present. For example, sodium chloride (Figure 4.24) consists of equal numbers of sodium and chlorine ions placed at alternate points of a simple cubic lattice, in such a way that each ion has six of the other kind of ions as its nearest neighbors.[17] This structure can be described as a face-centered cubic Bravais lattice with a basis consisting of a sodium ion at $0$ and a chlorine ion at the center of the conventional cubic cell, $(a/2)(\hat{x} + \hat{y} + \hat{z})$.



**Figure 4.24**
The sodium chloride structure. One type of ion is represented by black balls, the other type by white. The black and white balls form interpenetrating fcc lattices.

Table 4.5
**SOME COMPOUNDS WITH THE SODIUM CHLORIDE STRUCTURE**

| CRYSTAL | $a$ (Å) | CRYSTAL | $a$ (Å) | CRYSTAL | $a$ (Å) |
|---|---|---|---|---|---|
| LiF | 4.02 | RbF | 5.64 | CaS | 5.69 |
| LiCl | 5.13 | RbCl | 6.58 | CaSe | 5.91 |
| LiBr | 5.50 | RbBr | 6.85 | CaTe | 6.34 |
| LiI | 6.00 | RbI | 7.34 | SrO | 5.16 |
| NaF | 4.62 | CsF | 6.01 | SrS | 6.02 |
| NaCl | 5.64 | AgF | 4.92 | SrSe | 6.23 |
| NaBr | 5.97 | AgCl | 5.55 | SrTe | 6.47 |
| NaI | 6.47 | AgBr | 5.77 | BaO | 5.52 |
| KF | 5.35 | MgO | 4.21 | BaS | 6.39 |
| KCl | 6.29 | MgS | 5.20 | BaSe | 6.60 |
| KBr | 6.60 | MgSe | 5.45 | BaTe | 6.99 |
| KI | 7.07 | CaO | 4.81 | | |

## The Cesium Chloride Structure

Similarly, cesium chloride (Figure 4.25) consists of equal numbers of cesium and chlorine ions, placed at the points of a body-centered cubic lattice so that each ion

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[17]   For examples see Table 4.5.

has eight of the other kind as its nearest neighbors.[18] The translational symmetry of this structure is that of the simple cubic Bravais lattice, and it is described as a simple cubic lattice with a basis consisting of a cesium ion at the origin $0$ and a chlorine ion at the cube center $(a/2)(\hat{x} + \hat{y} + \hat{z})$.
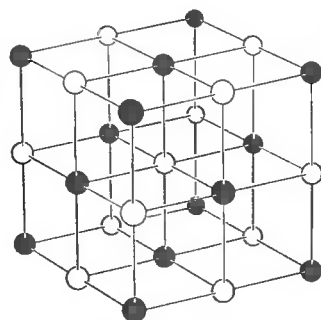
**Figure 4.25**
The cesium chloride structure. One type of ion is represented by black balls, the other type by white. The black and white balls form interpenetrating simple cubic lattices.
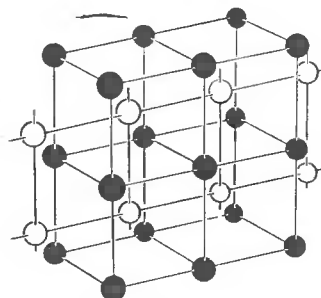


Table 4.6
**SOME COMPOUNDS WITH THE CESIUM CHLORIDE STRUCTURE**

| CRYSTAL | $a$ (Å) | CRYSTAL | $a$ (Å) |
|---------|---------|---------|---------|
| CsCl | 4.12 | TlCl | 3.83 |
| CsBr | 4.29 | TlBr | 3.97 |
| CsI | 4.57 | TlI | 4.20 |

## The Zincblende Structure

Zincblende has equal numbers of zinc and sulfur ions distributed on a diamond lattice so that each has four of the opposite kind as nearest neighbors (Figure 4.18). This structure[19] is an example of a lattice with a basis, which must be so described both because of the geometrical position of the ions and because two types of ions occur.

Table 4.7
**SOME COMPOUNDS WITH THE ZINCBLENDE STRUCTURE**

| CRYSTAL | $a$ (Å) | CRYSTAL | $a$ (Å) | CRYSTAL | $a$ (Å) |
|---------|---------|---------|---------|---------|---------|
| CuF | 4.26 | ZnS | 5.41 | AlSb | 6.13 |
| CuCl | 5.41 | ZnSe | 5.67 | GaP | 5.45 |
| CuBr | 5.69 | ZnTe | 6.09 | GaAs | 5.65 |
| CuI | 6.04 | CdS | 5.82 | GaSb | 6.12 |
| AgI | 6.47 | CdTe | 6.48 | InP | 5.87 |
| BeS | 4.85 | HgS | 5.85 | InAs | 6.04 |
| BeSe | 5.07 | HgSe | 6.08 | InSb | 6.48 |
| BeTe | 5.54 | HgTe | 6.43 | SiC | 4.35 |
| MnS (red) | 5.60 | AlP | 5.45 | | |
| MnSe | 5.82 | AlAs | 5.62 | | |

[18]  For examples see Table 4.6.
[19]  For example  \Table 4.7.

## OTHER ASPECTS OF CRYSTAL LATTICES

This chapter has concentrated on the description of the *translational* symmetry of crystal lattices in *real physical space*. Two other aspects of periodic arrays will be dealt with in subsequent chapters: in Chapter 5 we examine the consequences of translational symmetry not in real space, but in the so-called *reciprocal* (or *wave vector*) *space*, and in Chapter 7 we describe some features of the *rotational* symmetry of crystal lattices.

## PROBLEMS

**1.** In each of the following cases indicate whether the structure is a Bravais lattice. If it is, give three primitive vectors; if it is not, describe it as a Bravais lattice with as small as possible a basis.

(a)   Base-centered cubic (simple cubic with additional points in the centers of the horizontal faces of the cubic cell).

(b)   Side-centered cubic (simple cubic with additional points in the centers of the vertical faces of the cubic cell).

(c)   Edge-centered cubic (simple cubic with additional points at the midpoints of the lines joining nearest neighbors).

**2.** What is the Bravais lattice formed by all points with Cartesian coordinates $(n_1, n_2, n_3)$ if:

(a)   The $n_i$ are either all even or all odd?

(b)   The sum of the $n_i$ is required to be even?

**3.** Show that the angle between any two of the lines (bonds) joining a site of the diamond lattice to its four nearest neighbors is $\cos^{-1}(-1/3) = 109°28'$.

**4.** (a)   Prove that the Wigner-Seitz cell for any two-dimensional Bravais lattice is either a hexagon or a rectangle.

(b)   Show that the ratio of the lengths of the diagonals of each parallelogram face of the Wigner-Seitz cell for the face-centered cubic lattice (Figure 4.16) is $\sqrt{2}:1$.

(c)   Show that every edge of the polyhedron bounding the Wigner-Seitz cell of the body-centered cubic lattice (Figure 4.15) is $\sqrt{2}/4$ times the length of the conventional cubic cell.

(d)   Prove that the hexagonal faces of the bcc Wigner-Seitz cell are all regular hexagons. (Note that the axis perpendicular to a hexagonal face passing through its center has only threefold symmetry, so this symmetry alone is not enough.)

**5.** (a)   Prove that the ideal $c/a$ ratio for the hexagonal close-packed structure is $\sqrt{8/3} = 1.633$.

(b)   Sodium transforms from bcc to hcp at about 23K (the "martensitic" transformation). Assuming that the density remains fixed through this transition, find the lattice constant $a$ of the hexagonal phase, given that $a = 4.23$ Å in the cubic phase and that the $c/a$ ratio is indistinguishable from its ideal value.

**6.** The face-centered cubic is the most dense and the simple cubic is the least dense of the three cubic Bravais lattices. The diamond structure is less dense than any of these. One measure of this is that the coordination numbers are: fcc, 12; bcc, 8; sc, 6; diamond, 4. Another is the following: Suppose identical solid spheres are distributed through space in su    way that their centers

lie on the points of each of these four structures, and spheres on neighboring points just touch, without overlapping. (Such an arrangement of spheres is called a close-packing arrangement.) Assuming that the spheres have unit density, show that the density of a set of close-packed spheres on each of the four structures (the "packing fraction") is:

$$
\begin{aligned}
\text{fcc:} && \sqrt{2}\pi/6 &= 0.74 \\
\text{bcc:} && \sqrt{3}\pi/8 &= 0.68 \\
\text{sc:} && \pi/6 &= 0.52 \\
\text{diamond:} && \sqrt{3}\pi/16 &= 0.34.
\end{aligned}
$$

7. Let $N_n$ be the number of $n$th nearest neighbors of a given Bravais lattice point (e.g., in a simple cubic Bravais lattice $N_1 = 6$, $N_2 = 12$, etc.). Let $r_n$ be the distance to the $n$th nearest neighbor expressed as a multiple of the nearest neighbor distance (e.g., in a simple cubic Bravais lattice $r_1 = 1, r_2 = \sqrt{2} = 1.414$). Make a table of $N_n$ and $r_n$ for $n = 1, ..., 6$ for the fcc, bcc, and sc Bravais lattices.

8. (a) Given a Bravais lattice, let $a_1$ be a vector joining a particular point $P$ to one of its nearest neighbors. Let $P'$ be a lattice point not on the line through $P$ in the direction of $a_1$ that is as close to the line as any other lattice point, and let $a_2$ join $P$ to $P'$. Let $P''$ be a lattice point not on the plane through $P$ determined by $a_1$ and $a_2$ that is as close to the plane as any other lattice point, and let $a_3$ join $P$ to $P''$. Prove that $a_1$, $a_2$, and $a_3$ are a set of primitive vectors for the Bravais lattice.

(b) Prove that a Bravais lattice can be defined as a discrete set of vectors, not all in a plane, closed under addition and subtraction (as described on page 70).

# 5
# *The Reciprocal Lattice*

Definitions and Examples

First Brillouin Zone

Lattice Planes and Miller Indices

The reciprocal lattice plays a fundamental role in most analytic studies of periodic structures. One is led to it from such diverse avenues as the theory of crystal diffraction, the abstract study of functions with the periodicity of a Bravais lattice, or the question of what can be salvaged of the law of momentum conservation when the full translational symmetry of free space is reduced to that of a periodic potential. In this brief chapter we shall describe some important elementary features of the reciprocal lattice from a general point of view not tied to any particular application.

## DEFINITION OF RECIPROCAL LATTICE

Consider a set of points $\mathbf{R}$ constituting a Bravais lattice, and a plane wave, $e^{i\mathbf{k}\cdot\mathbf{r}}$. For general k, such a plane wave will not, of course, have the periodicity of the Bravais lattice, but for certain special choices of wave vector it will. *The set of all wave vectors $\mathbf{K}$ that yield plane waves with the periodicity of a given Bravais lattice is known as its reciprocal lattice.* Analytically, K belongs to the reciprocal lattice of a Bravais lattice of points R, provided that the relation

$$e^{i\mathbf{K}\cdot(\mathbf{r}+\mathbf{R})} = e^{i\mathbf{K}\cdot\mathbf{r}} \tag{5.1}$$

holds for any r, and for all R in the Bravais lattice. Factoring out $e^{i\mathbf{K}\cdot\mathbf{r}}$, we can characterize the reciprocal lattice as the set of wave vectors K satisfying

$$e^{i\mathbf{K}\cdot\mathbf{R}} = 1 \tag{5.2}$$

for all R in the Bravais lattice.

Note that a reciprocal lattice is defined with reference to a particular Bravais lattice. The Bravais lattice that determines a given reciprocal lattice is often referred to as the *direct lattice*, when viewed in relation to its reciprocal. Note also that although one could define a set of vectors K satisfying (5.2) for an arbitrary set of vectors R, such a set of K is called a reciprocal lattice only if the set of vectors R is a Bravais lattice.[1]

## THE RECIPROCAL LATTICE IS A BRAVAIS LATTICE

That the reciprocal lattice is itself a Bravais lattice follows most simply from the definition of a Bravais lattice given in footnote 7 of Chapter 4, along with the fact that if $\mathbf{K}_1$ and $\mathbf{K}_2$ satisfy (5.2), so, obviously, will their sum and difference.

It is worth considering a more clumsy proof of this fact, which provides an explicit algorithm for constructing the reciprocal lattice. Let $\mathbf{a}_1, \mathbf{a}_2$, and $\mathbf{a}_3$ be a set of primitive vectors for the direct lattice. Then the reciprocal lattice can be generated by the three primitive vectors

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)},$$

$$\mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}, \tag{5.3}$$

$$\mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}.$$

---

[1]  In particular, in working with a lattice with a basis one uses the reciprocal lattice determined by the underlying Bravais lattice, rather than a set of K satisfying (5.2) for v    R describing both the Bravais lattice and the basis points.

To verify that (5.3) gives a set of primitive vectors for the reciprocal lattice, one first notes that the $b_i$ satisfy[2]

$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij}, \tag{5.4}$$

where $\delta_{ij}$ is the Kronecker delta symbol:

$$\begin{aligned} \delta_{ij} &= 0, & i \neq j; \\ \delta_{ij} &= 1, & i = j. \end{aligned} \tag{5.5}$$

Now any vector $\mathbf{k}$ can be written as a linear combination[3] of the $b_i$:

$$\mathbf{k} = k_1\mathbf{b}_1 + k_2\mathbf{b}_2 + k_3\mathbf{b}_3. \tag{5.6}$$

If $\mathbf{R}$ is any direct lattice vector, then

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3, \tag{5.7}$$

where the $n_i$ are integers. It follows from (5.4) that

$$\mathbf{k} \cdot \mathbf{R} = 2\pi(k_1n_1 + k_2n_2 + k_3n_3). \tag{5.8}$$

For $e^{i\mathbf{k}\cdot\mathbf{R}}$ to be unity for all $\mathbf{R}$ (Eq. (5.2)) $\mathbf{k} \cdot \mathbf{R}$ must be $2\pi$ times an integer for any choices of the integers $n_i$. This requires the coefficients $k_i$ to be integers. Thus the condition (5.2) that $\mathbf{K}$ be a reciprocal lattice vector is satisfied by just those vectors that are linear combinations (5.6) of the $b_i$ with integral coefficients. Thus (compare Eq. (4.1)) the reciprocal lattice is a Bravais lattice and the $b_i$ can be taken as primitive vectors.

## THE RECIPROCAL OF THE RECIPROCAL LATTICE

Since the reciprocal lattice is itself a Bravais lattice, one can construct *its* reciprocal lattice. This turns out to be nothing but the original direct lattice.

One way to prove this is by constructing $\mathbf{c}_1$, $\mathbf{c}_2$, and $\mathbf{c}_3$ out of the $b_i$ according to the same formula (5.3) by which the $b_i$ were constructed from the $a_i$. It then follows from simple vector identities (Problem 1) that $\mathbf{c}_i = \mathbf{a}_i$, $i = 1, 2, 3$.

A simpler proof follows from the observation that according to the basic definition (5.2), the reciprocal of the reciprocal lattice is the set of all vectors $\mathbf{G}$ satisfying

$$e^{i\mathbf{G}\cdot\mathbf{K}} = 1 \tag{5.9}$$

for all $\mathbf{K}$ in the reciprocal lattice. Since any direct lattice vector $\mathbf{R}$ has this property (again by (5.2)), all direct lattice vectors are in the lattice reciprocal to the reciprocal lattice. Furthermore, no other vectors can be, for a vector not in the direct lattice has the form $\mathbf{r} = x_1\mathbf{a}_1 + x_2\mathbf{a}_2 + x_3\mathbf{a}_3$ with at least one nonintegral $x_l$. For that value of $i$, $e^{i\mathbf{b}_i\cdot\mathbf{r}} = e^{2\pi i x_i} \neq 1$, and condition (5.9) is violated for the reciprocal lattice vector $\mathbf{K} = \mathbf{b}_l$.

---

[2]   When $i \neq j$, Eq. (5.4) follows because the cross product of two vectors is normal to both. When $i = j$, it follows because of the vector identity

$$\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3) = \mathbf{a}_2 \cdot (\mathbf{a}_3 \times \mathbf{a}_1) = \mathbf{a}_3 \cdot (\mathbf{a}_1 \times \mathbf{a}_2).$$

[3]   This is t      or any three vectors not all in one plane. It is easy to verify that the $b_i$ are not all in a plane as long as the $a_i$ are not.

## IMPORTANT EXAMPLES

The *simple cubic* Bravais lattice, with cubic primitive cell of side $a$, has as its reciprocal a simple cubic lattice with cubic primitive cell of side $2\pi/a$. This can be seen, for example, from the construction (5.3), for if

$$\mathbf{a}_1 = a\hat{\mathbf{x}}, \quad \mathbf{a}_2 = a\hat{\mathbf{y}}, \quad \mathbf{a}_3 = a\hat{\mathbf{z}}, \tag{5.10}$$

then

$$\mathbf{b}_1 = \frac{2\pi}{a}\hat{\mathbf{x}}, \quad \mathbf{b}_2 = \frac{2\pi}{a}\hat{\mathbf{y}}, \quad \mathbf{b}_3 = \frac{2\pi}{a}\hat{\mathbf{z}}. \tag{5.11}$$

The *face-centered cubic* Bravais lattice with conventional cubic cell of side $a$ has as its reciprocal a body-centered cubic lattice with conventional cubic cell of side $4\pi/a$. This can be seen by applying the construction (5.3) to the fcc primitive vectors (4.5). The result is

$$\mathbf{b}_1 = \frac{4\pi}{a}\frac{1}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}} - \hat{\mathbf{x}}), \quad \mathbf{b}_2 = \frac{4\pi}{a}\frac{1}{2}(\hat{\mathbf{z}} + \hat{\mathbf{x}} - \hat{\mathbf{y}}), \quad \mathbf{b}_3 = \frac{4\pi}{a}\frac{1}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}}) \tag{5.12}$$

This has precisely the form of the bcc primitive vectors (4.4), provided that the side of the cubic cell is taken to be $4\pi/a$.

The *body-centered cubic* lattice with conventional cubic cell of side $a$ has as its reciprocal a face-centered cubic lattice with conventional cubic cell of side $4\pi/a$. This can again be proved from the construction (5.3), but it also follows from the above result for the reciprocal of the fcc lattice, along with the theorem that the reciprocal of the reciprocal is the original lattice.

It is left as an exercise for the reader to verify (Problem 2) that the reciprocal to a *simple hexagonal* Bravais lattice with lattice constants $c$ and $a$ (Figure 5.1a) is another
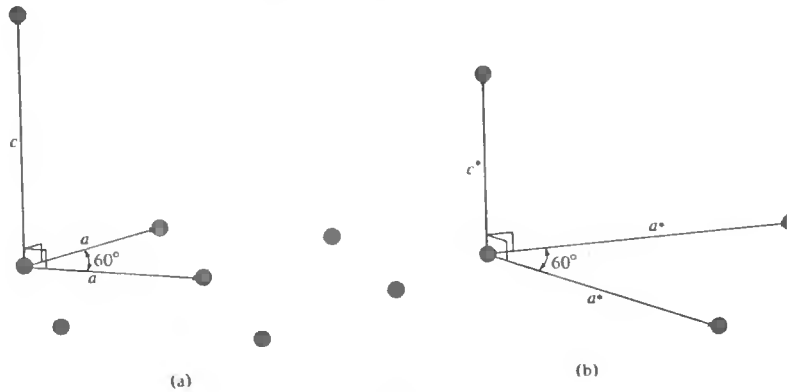


(a)    (b)

**Figure 5.1**
(a) Primitive vectors for the simple hexagonal Bravais lattice. (b) Primitive vectors for the lattice reciprocal to that generated by the primitive vectors in (a). The $c$ and $c^*$ axes are parallel. The $a^*$ axes are rotated by 30° with respect to the $a$ axes in the plane perpendicular to the $c$ or $c^*$ axes. The reciprocal lattice is also simple hexagonal.

simple hexagonal lattice with lattice constants $2\pi/c$ and $4\pi/\sqrt{3}a$ (Figure 5.1b), rotated through $30°$ about the $c$-axis with respect to the direct lattice.[4]

## VOLUME OF THE RECIPROCAL LATTICE PRIMITIVE CELL

If $v$ is the volume[5] of a primitive cell in the direct lattice, then the primitive cell of the reciprocal lattice has a volume $(2\pi)^3/v$. This is proved in Problem 1.

## FIRST BRILLOUIN ZONE

The Wigner-Seitz primitive cell (page 73) of the reciprocal lattice is known as the *first Brillouin zone*. As the name suggests, one also defines higher Brillouin zones, which are primitive cells of a different type that arise in the theory of electronic levels in a periodic potential. They are described in Chapter 9.

Although the terms "Wigner-Seitz cell" and "first Brillouin zone" refer to identical geometrical constructions, in practice the latter term is applied only to the $k$-space cell. In particular, when reference is made to the first Brillouin zone of a particular $r$-space Bravais lattice (associated with a particular crystal structure), what is always meant is the Wigner-Seitz cell of the associated reciprocal lattice. Thus, because the reciprocal of the body-centered cubic lattice is face-centered cubic, the first Brillouin zone of the bcc lattice (Figure 5.2a) is just the fcc Wigner-Seitz cell (Figure 4.16). Conversely, the first Brillouin zone of the fcc lattice (Figure 5.2b) is just the bcc Wigner-Seitz cell (Figure 4.15).

**Figure 5.2**
(a) The first Brillouin zone for the body-centered cubic lattice.
(b) The first Brillouin zone for the face-centered cubic lattice.



(a)  (b)
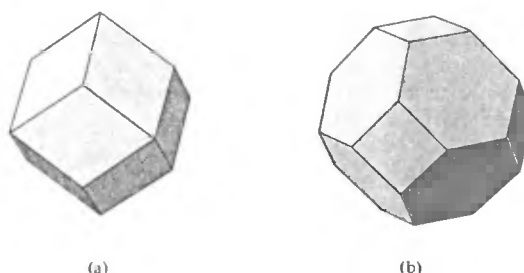
## LATTICE PLANES

There is an intimate relation between vectors in the reciprocal lattice and planes of points in the direct lattice. This relation is of some importance in understanding the fundamental role the reciprocal lattice plays in the theory of diffraction, and will be applied to that problem in the next chapter. Here we shall describe the relation in general geometrical terms.

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[4] The hexagonal close-packed *structure* is not a Bravais lattice, and therefore the reciprocal lattice used in the analysis of hcp solids is that of the simple hexagonal lattice (see footnote 1).

[5] The primitive cell volume is independent of the choice of cell, as proved in Chapter 4.

Given a particular Bravais lattice, a *lattice plane* is defined to be any plane containing at least three noncollinear Bravais lattice points. Because of the translational symmetry of the Bravais lattice, any such plane will actually contain infinitely many lattice points, which form a two-dimensional Bravais lattice within the plane. Some lattice planes in a simple cubic Bravais lattice are pictured in Figure 5.3.
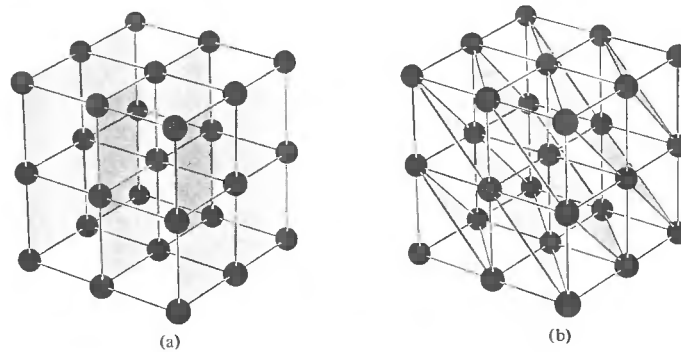


(a)   (b)

**Figure 5.3**
Some lattice planes (shaded) in a simple cubic Bravais lattice: (a) and (b) show two different ways of representing the lattice as a family of lattice planes.

By a *family of lattice planes* we mean a set of parallel, equally spaced lattice planes, which together contain all the points of the three-dimensional Bravais lattice. Any lattice plane is a member of such a family. Evidently the resolution of a Bravais lattice into a family of lattice planes is far from unique (Figure 5.3). The reciprocal lattice provides a very simple way to classify all possible families of lattice planes, which is embodied in the following theorem:

> For any family of lattice planes separated by a distance $d$, there are reciprocal lattice vectors perpendicular to the planes, the shortest of which have a length of $2\pi/d$. Conversely, for any reciprocal lattice vector $\mathbf{K}$, there is a family of lattice planes normal to $\mathbf{K}$ and separated by a distance $d$, where $2\pi/d$ is the length of the shortest reciprocal lattice vector parallel to $\mathbf{K}$.

The theorem is a straightforward consequence of (a) the definition (5.2) of reciprocal lattice vectors as the wave vectors of plane waves that are unity at all Bravais lattice sites and (b) the fact that a plane wave has the same value at all points lying in a family of planes that are perpendicular to its wave vector and separated by an integral number of wavelengths.

To prove the first part of the theorem, given a family of lattice planes, let $\hat{\mathbf{n}}$ be a unit vector normal to the planes. That $\mathbf{K} = 2\pi\hat{\mathbf{n}}/d$ is a reciprocal lattice vector follows from the fact that the plane wave $e^{i\mathbf{K} \cdot \mathbf{r}}$ is constant in planes perpendicular to $\mathbf{K}$ and has the same value in planes separated by $\lambda = 2\pi/K = d$. Since one of the lattice planes contains the Bravais lattice point $\mathbf{r} = 0$, $e^{i\mathbf{K} \cdot \mathbf{r}}$ must be unity for any point $\mathbf{r}$ in any of the planes. Since the planes contain all Bravais lattice points, $e^{i\mathbf{K} \cdot \mathbf{r}} = 1$ for all $\mathbf{R}$, so that $\mathbf{K}$ is indeed a reciprocal lattice vector. Furthermore, $\mathbf{K}$ is the shortest

reciprocal lattice vector normal to the planes, for any wave vector shorter than $\mathbf{K}$ will give a plane wave with wavelength greater than $2\pi/K = d$. Such a plane wave cannot have the same value on all planes in the family, and therefore cannot give a plane wave that is unity at all Bravais lattice points.

To prove the converse of the theorem, given a reciprocal lattice vector, let $\mathbf{K}$ be the shortest parallel reciprocal lattice vector. Consider the set of real space planes on which the plane wave $e^{i\mathbf{K}\cdot\mathbf{r}}$ has the value unity. These planes (one of which contains the point $\mathbf{r} = 0$) are perpendicular to $\mathbf{K}$ and separated by a distance $d = 2\pi/K$. Since the Bravais lattice vectors $\mathbf{R}$ all satisfy $e^{i\mathbf{K}\cdot\mathbf{R}} = 1$ for any reciprocal lattice vector $\mathbf{K}$, they must all lie within these planes; i.e., the family of planes must contain within it a family of lattice planes. Furthermore the spacing between the lattice planes is also $d$ (rather than some integral multiple of $d$), for if only every $n$th plane in the family contained Bravais lattice points, then according to the first part of the theorem, the vector normal to the planes of length $2\pi/nd$, i.e., the vector $\mathbf{K}/n$, would be a reciprocal lattice vector. This would contradict our original assumption that no reciprocal lattice vector parallel to $\mathbf{K}$ is shorter than $\mathbf{K}$.

## MILLER INDICES OF LATTICE PLANES

The correspondence between reciprocal lattice vectors and families of lattice planes provides a convenient way to specify the orientation of a lattice plane. Quite generally one describes the orientation of a plane by giving a vector normal to the plane. Since we know there are reciprocal lattice vectors normal to any family of lattice planes, it is natural to pick a reciprocal lattice vector to represent the normal. To make the choice unique, one uses the shortest such reciprocal lattice vector. In this way one arrives at the *Miller indices* of the plane:

The Miller indices of a lattice plane are the coordinates of the shortest reciprocal lattice vector normal to that plane, with respect to a specified set of primitive reciprocal lattice vectors. Thus a plane with Miller indices $h, k, l$, is normal to the reciprocal lattice vector $h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$.

As so defined, the Miller indices are integers, since any reciprocal lattice vector is a linear combination of three primitive vectors with integral coefficients. Since the normal to the plane is specified by the shortest perpendicular reciprocal lattice vector, the integers $h, k, l$ can have no common factor. Note also that the Miller indices depend on the particular choice of primitive vectors.

In simple cubic Bravais lattices the reciprocal lattice is also simple cubic and the Miller indices are the coordinates of a vector normal to the plane in the obvious cubic coordinate system. As a general rule, face-centered and body-centered cubic Bravais lattice are described in terms of a conventional cubic cell, i.e., as simple cubic lattices with bases. Since any lattice plane in a fcc or bcc lattice is also a lattice plane in the underlying simple cubic lattice, the same elementary cubic indexing can be used to specify lattice planes. In practice, it is only in the description of noncubic crystals that one must remember that the Miller indices are the coordinates of the normal in a system given by the reciprocal lattice, rather than the direct lattice.

The Miller indices of a plane have a geometrical interpretation in the direct lattice, which is sometimes offered as an alternative way of defining them. Because a lattice

plane with Miller indices $h$, $k$, $l$ is perpendicular to the reciprocal lattice vector $\mathbf{K} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$, it will be contained in the continuous plane $\mathbf{K} \cdot \mathbf{r} = A$, for suitable choice of the constant $A$. This plane intersects the axes determined by the direct lattice primitive vectors $\mathbf{a}_i$ at the points $x_1\mathbf{a}_1$, $x_2\mathbf{a}_2$, and $x_3\mathbf{a}_3$ (Figure 5.4), where the $x_i$ are determined by the condition that $x_i\mathbf{a}_i$ indeed satisfy the equation of the plane: $\mathbf{K} \cdot (x_i\mathbf{a}_i) = A$. Since $\mathbf{K} \cdot \mathbf{a}_1 = 2\pi h$, $\mathbf{K} \cdot \mathbf{a}_2 = 2\pi k$, and $\mathbf{K} \cdot \mathbf{a}_3 = 2\pi l$, it follows that

$$x_1 = \frac{A}{2\pi h}, \quad x_2 = \frac{A}{2\pi k}, \quad x_3 = \frac{A}{2\pi l}. \tag{5.13}$$

Thus the intercepts with the crystal axes of a lattice plane are inversely proportional to the Miller indices of the plane.
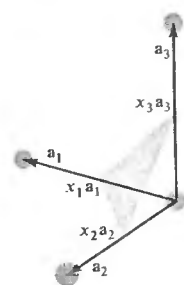


**Figure 5.4**
An illustration of the crystallographic definition of the Miller indices of a lattice plane. The shaded plane can be a portion of the continuous plane in which the points of the lattice plane lie, or any plane parallel to the lattice plane. The Miller indices are inversely proportional to the $x_i$.

Crystallographers put the cart before the horse, *defining* the Miller indices to be a set of integers with no common factors, inversely proportional to the intercepts of the crystal plane along the crystal axes:

$$h{:}k{:}l = \frac{1}{x_1}{:}\frac{1}{x_2}{:}\frac{1}{x_3}. \tag{5.14}$$

## SOME CONVENTIONS FOR SPECIFYING DIRECTIONS

Lattice planes are usually specified by giving their Miller indices in parentheses: $(h, k, l)$. Thus, in a cubic system, a plane with a normal $(4, -2, 1)$ (or, from the crystallographic viewpoint, a plane with intercepts $(1, -2, 4)$ along cubic axes) is called a $(4, -2, 1)$ plane. The commas are eliminated without confusion by writing $\bar{n}$ instead of $-n$, simplifying the description to $(4\bar{2}1)$. One must know what set of axes is being used to interpret these symbols unambiguously. Simple cubic axes are invariably used when the crystal has cubic symmetry. Some examples of planes in cubic crystals are shown in Figure 5.5.

A similar convention is used to specify directions in the direct lattice, but to avoid confusion with the Miller indices (directions in the reciprocal lattice) square brackets are used instead of parentheses. Thus the body diagonal of a simple cubic lattice lies in the [111] direction and, in general the lattice point $n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$ lies in the direction $[n_1n_2n_3]$ from the origin.

There is also a notation specifying both a family of lattice planes and all those other families that are equivalent to it by virtue of the symmetry of the crystal. Thus
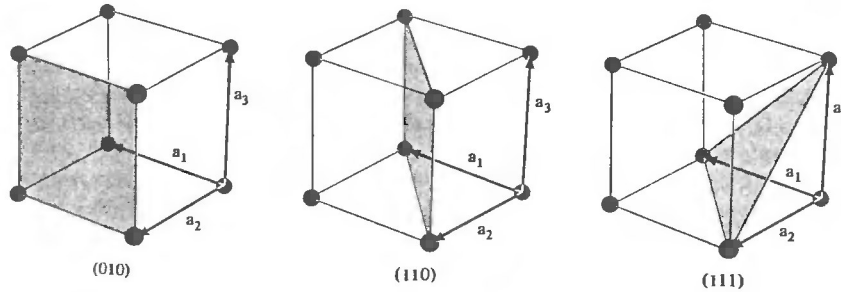
**Figure 5.5**
Three lattice planes and their Miller indices in a simple cubic Bravais lattice.

the (100), (010), and (001) planes are all equivalent in a cubic crystal. One refers to them collectively as the $\{100\}$ planes, and in general one uses $\{hkl\}$ to refer to the $(hkl)$ planes and all those that are equivalent to them by virtue of the crystal symmetry. A similar convention is used with directions: the $[100]$, $[010]$, $[001]$, $[\bar{1}00]$, $[0\bar{1}0]$, and $[00\bar{1}]$ directions in a cubic crystal are referred to, collectively, as the $\langle 100 \rangle$ directions.

This concludes our general geometrical discussion of the reciprocal lattice. In Chapter 6 we shall see an important example of the utility and the power of the concept in the theory of the diffraction of X rays by a crystal.

## PROBLEMS

**1.** (a) Prove that the reciprocal lattice primitive vectors defined in (5.3) satisfy

$$\mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3) = \frac{(2\pi)^3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}. \tag{5.15}$$

(*Hint:* Write $\mathbf{b}_1$ (but not $\mathbf{b}_2$ or $\mathbf{b}_3$) in terms of the $\mathbf{a}_i$, and use the orthogonality relations (5.4).)

(b) Suppose primitive vectors are constructed from the $\mathbf{b}_i$ in the same manner (Eq. (5.3)) as the $\mathbf{b}_i$ are constructed from the $\mathbf{a}_i$. Prove that these vectors are just the $\mathbf{a}_i$ themselves; i.e., show that

$$2\pi \frac{\mathbf{b}_2 \times \mathbf{b}_3}{\mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3)} = \mathbf{a}_1, \quad \text{etc.} \tag{5.16}$$

(*Hint:* Write $\mathbf{b}_3$ in the numerator (but not $\mathbf{b}_2$) in terms of the $\mathbf{a}_i$, use the vector identity $\mathbf{A} \times (\mathbf{B} \times \mathbf{C}) = \mathbf{B}(\mathbf{A} \cdot \mathbf{C}) - \mathbf{C}(\mathbf{A} \cdot \mathbf{B})$, and appeal to the orthogonality relations (5.4) and the result (5.15) above.)

(c) Prove that the volume of a Bravais lattice primitive cell is

$$v = |\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)|, \tag{5.17}$$

where the $\mathbf{a}_i$ are three primitive vectors. (In conjunction with (5.15) this establishes that the volume of the reciprocal lattice primitive cell is $(2\pi)^3/v$.)

**2.** (a)   Using the primitive vectors given in Eq. (4.9) and the construction (5.3) (or by any other method) show that the reciprocal of the simple hexagonal Bravais lattice is also simple hexagonal, with lattice constants $2\pi/c$ and $4\pi/\sqrt{3}a$, rotated through 30° about the $c$-axis with respect to the direct lattice.

(b)   For what value of $c/a$ does the ratio have the same value in both direct and reciprocal lattices? If $c/a$ is ideal in the direct lattice, what is its value in the reciprocal lattice?

(c)   The Bravais lattice generated by three primitive vectors of equal length $a$, making equal angles $\theta$ with one another, is known as the trigonal Bravais lattice (see Chapter 7). Show that the reciprocal of a trigonal Bravais lattice is also trigonal, with an angle $\theta^*$ given by $-\cos\theta^* = \cos\theta/[1 + \cos\theta]$, and a primitive vector length $a^*$, given by $a^* = (2\pi/a)(1 + 2\cos\theta\cos\theta^*)^{-1/2}$.

**3.** (a)   Show that the density of lattice points (per unit area) in a lattice plane is $d/v$, where $v$ is the primitive cell volume and $d$ the spacing between neighboring planes in the family to which the given plane belongs.

(b)   Prove that the lattice planes with the greatest densities of points are the $\{111\}$ planes in a face-centered cubic Bravais lattice and the $\{110\}$ planes in a body-centered cubic Bravais lattice. (*Hint:* This is most easily done by exploiting the relation between families of lattice planes and reciprocal lattice vectors.)

**4.** Prove that any reciprocal lattice vector $\mathbf{K}$ is an integral multiple of the shortest parallel reciprocal lattice vector $\mathbf{K_0}$. (Hint: Assume the contrary, and deduce that since the reciprocal lattice is a Bravais lattice, there must be a reciprocal lattice vector parallel to $\mathbf{K}$ shorter than $\mathbf{K_0}$.)