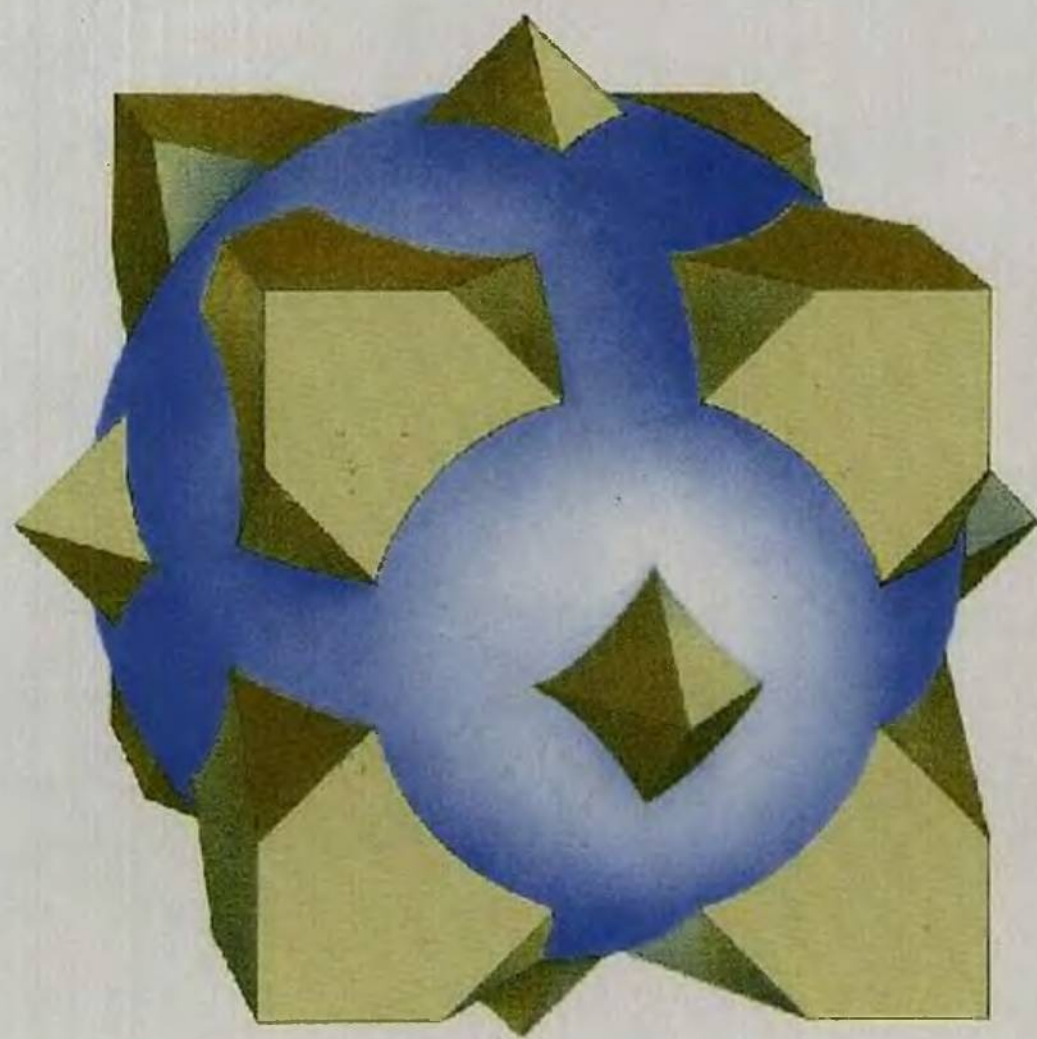


ASHCROFT / MERMIN



SOLID STATE PHYSICS

4

Crystal Lattices

1

Bravais Lattice and Primitive Vectors

Simple, Body-Centered, and Face-Centered
Cubic Lattices

Primitive Unit Cell, Wigner-Seitz Cell, and
Conventional Cell

Crystal Structures and Lattices with Bases

Hexagonal Close-Packed and Diamond Structures

Sodium Chloride, Cesium Chloride, and
Zincblende Structures

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 lattice²:

- (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 \mathbf{R} of the form

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

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 steps⁴ 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.

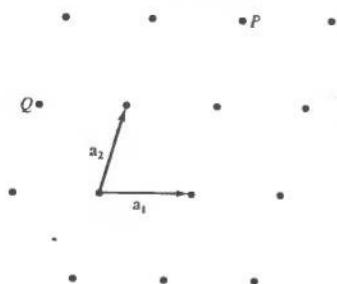


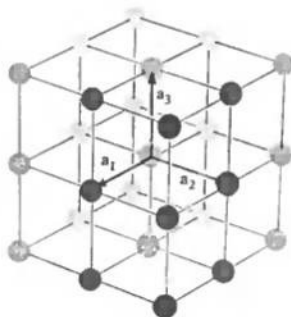
Figure 4.1

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.



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*.

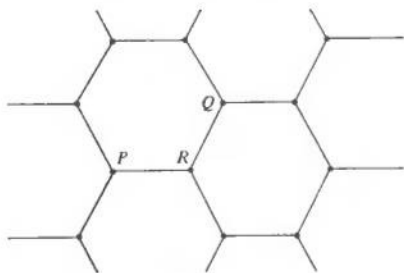


Figure 4.3

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 \mathbf{a}_1 , \mathbf{a}_2 , and \mathbf{a}_3 , one usually considers the finite lattice of N sites to be the set of points of the form $\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$, where $0 \leq n_1 < N_1$, $0 \leq n_2 < N_2$, $0 \leq n_3 < N_3$, and $N = N_1N_2N_3$. This artifact is closely connected with the generalization to the description of crystalline systems⁶ 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

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.

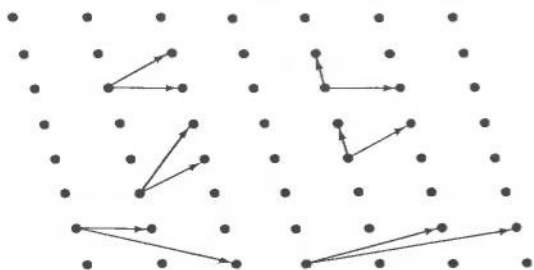
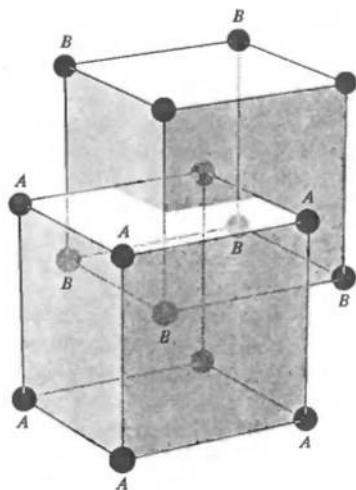


Figure 4.4
Several possible choices of pairs of primitive vectors for a two-dimensional Bravais lattice. They are drawn, for clarity, from different origins.

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

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

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)

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

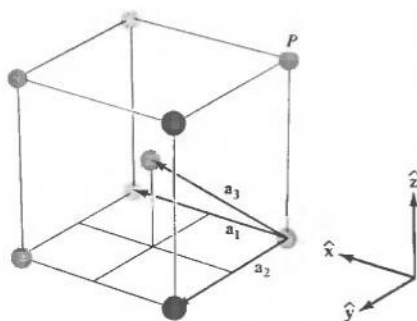


Figure 4.6

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

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

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

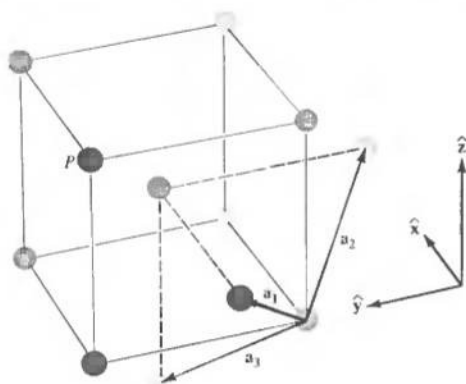


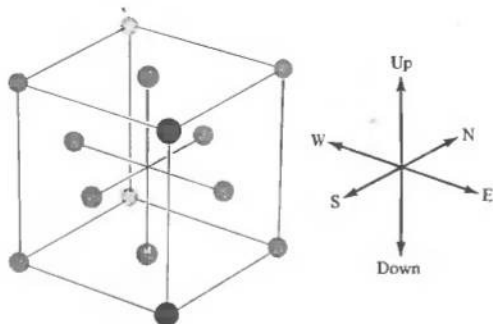
Figure 4.7

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.

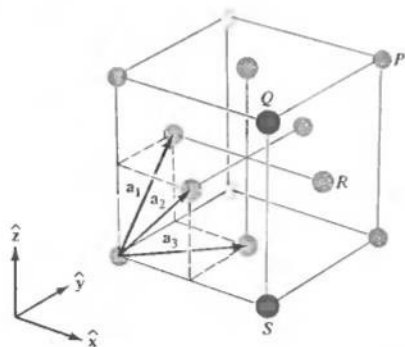
In the same way one can also regard the simple cubic lattice as being composed of all points centering the north-south faces of the original simple cubic lattice, or all points centering the east-west faces of the original cubic lattice. In either case the remaining points will be found centered on the 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

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

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)	δ -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
β -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 \mathbf{R} determines a *translation* or *displacement*, in which everything is moved bodily through space by a distance R in the direction of \mathbf{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

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 coordination 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.

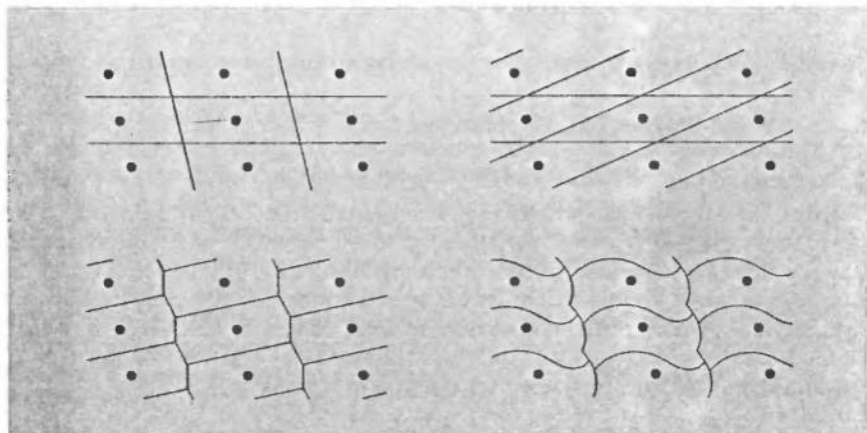


Figure 4.10

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 lattice⁹ and v is the volume of the primitive cell, then $nv = 1$. Thus $v = 1/n$. Since

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 symbols.

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.

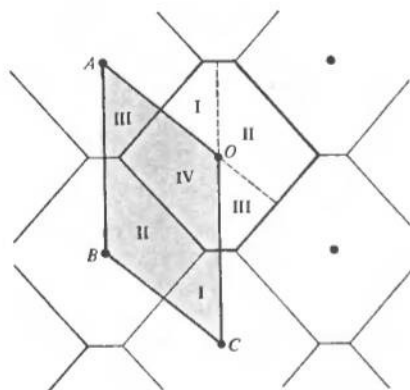


Figure 4.11

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— \vec{CO} ; Region II— \vec{BO} ; Region III— \vec{AO} ; Region IV—no translation.

The obvious primitive cell to associate with a particular set of primitive vectors, $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$, is the set of all points \mathbf{r} of the form

$$\mathbf{r} = x_1 \mathbf{a}_1 + x_2 \mathbf{a}_2 + x_3 \mathbf{a}_3 \quad (4.6)$$

for all x_i ranging continuously between 0 and 1; i.e., the parallelepiped spanned by the three vectors $\mathbf{a}_1, \mathbf{a}_2$, and \mathbf{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 parallelepiped, 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:

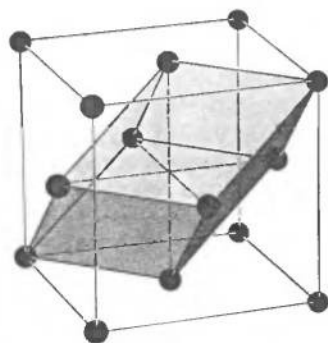


Figure 4.12

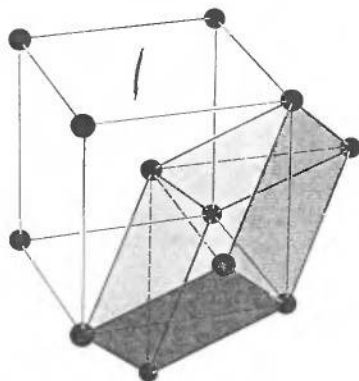
Primitive and conventional unit cells for the face-centered cubic Bravais lattice. The conventional cell is the large cube. The primitive cell is the figure with six parallelogram faces. It has one quarter the volume of the cube, and rather less symmetry.

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 neighbor¹¹ it will belong to the Wigner-Seitz cell of precisely one lattice point. It follows that a

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 others¹³ in the lattice, bisecting each line

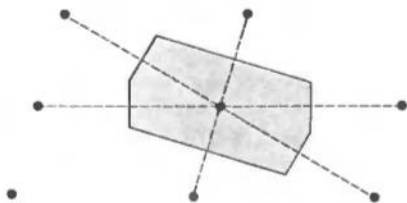


Figure 4.14

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).

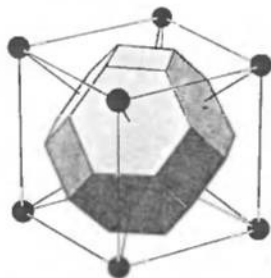
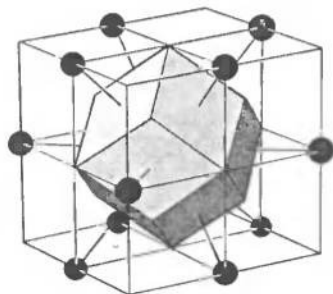


Figure 4.16

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 y^i planes 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 crystal¹⁴ 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 lattice¹⁵ 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.

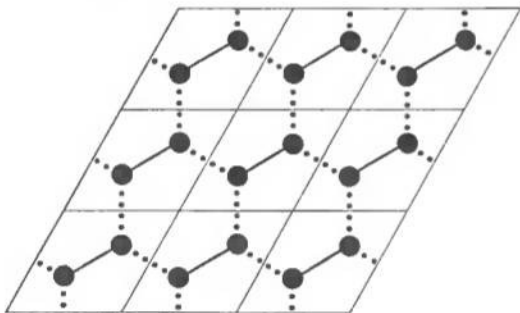


Figure 4.17

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

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

or a four-point basis

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

¹⁴ But still idealized in being infinite in extent.

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

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 \mathbf{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, \mathbf{K} belongs to the reciprocal lattice of a Bravais lattice of points \mathbf{R} , provided that the relation

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

holds for any \mathbf{r} , and for all \mathbf{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 \mathbf{K} satisfying

$$e^{i\mathbf{K}\cdot\mathbf{R}} = 1 \quad (5.2)$$

for all \mathbf{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 \mathbf{K} satisfying (5.2) for an arbitrary set of vectors \mathbf{R} , such a set of \mathbf{K} is called a reciprocal lattice only if the set of vectors \mathbf{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

$$\begin{aligned} \mathbf{b}_1 &= 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}, \\ \mathbf{b}_2 &= 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}, \\ \mathbf{b}_3 &= 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}. \end{aligned} \quad (5.3)$$

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 \mathbf{K} satisfying (5.2) for $\mathbf{r} = \mathbf{R} + \mathbf{r}_i$, \mathbf{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 \mathbf{b}_i satisfy²

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

where δ_{ij} is the Kronecker delta symbol:

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

Now any vector \mathbf{k} can be written as a linear combination³ of the \mathbf{b}_i :

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

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

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

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

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

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 2π 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 \mathbf{b}_i with integral coefficients. Thus (compare Eq. (4.1)) the reciprocal lattice is a Bravais lattice and the \mathbf{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 \mathbf{b}_i according to the same formula (5.3) by which the \mathbf{b}_i were constructed from the \mathbf{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

$$e^{i\mathbf{G} \cdot \mathbf{K}} = 1 \quad (5.9)$$

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_i . 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 $\mathbf{K} = \mathbf{b}_i$.

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 true for any three vectors not all in one plane. It is easy to verify that the \mathbf{b}_i are not all in a plane as long as the \mathbf{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

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

then

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

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

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

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

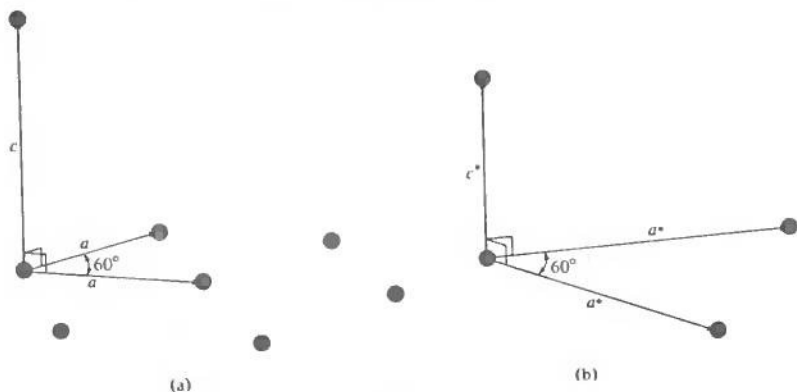


Figure 5.1

(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 volume⁵ 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.

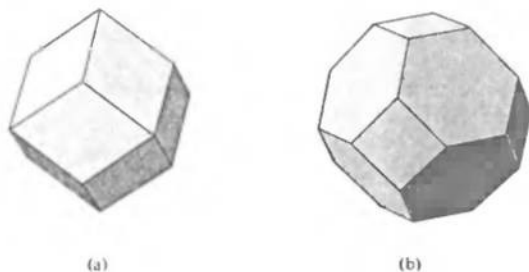
FIRST BRILLOUIN ZONE

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.



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.

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.

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