From:

Solid State Physics

Ashcroft & Mermin

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4
Crystal Lattices

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 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

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3,$$ (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 $\sum n_i\mathbf{a}_i$ 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.
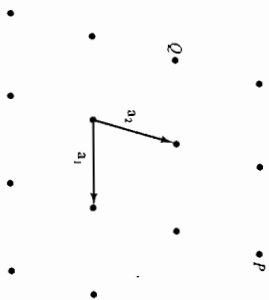
Figure 4.1
A general two-dimensional Bravais lattice of no particular symmetry: the oblique net. Primitive vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ are shown. All points in the net are linear combinations of these with integral coefficients; for example, $P = \mathbf{a}_1 + 2\mathbf{a}_2$, and $Q = -\mathbf{a}_1 + \mathbf{a}_2$.

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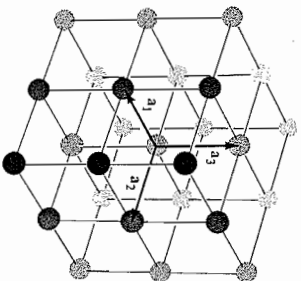
[3] We continue with the convention that "integer" means a negative integer or zero, as well as a positive integer.

[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.

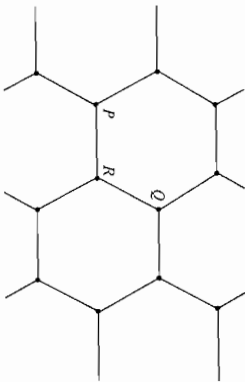[5] A two-dimensional Bravais lattice is also known as a *net*.

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 $0 \leq n_1 < N_1$, $0 \leq n_2 < N_2$, $0 \leq n_3 < N_3$, 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.
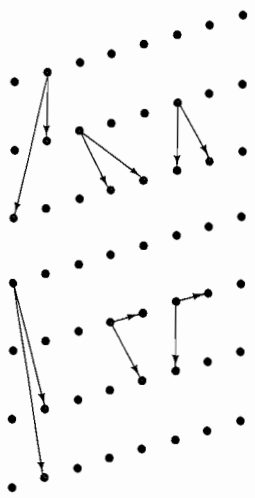

Figure 4.4
Several possible choices of pairs of primitive vectors for a two-dimensional Bravais lattice. They are drawn, for clarity, from different origins.

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 do corner points of a second simple cubic array.
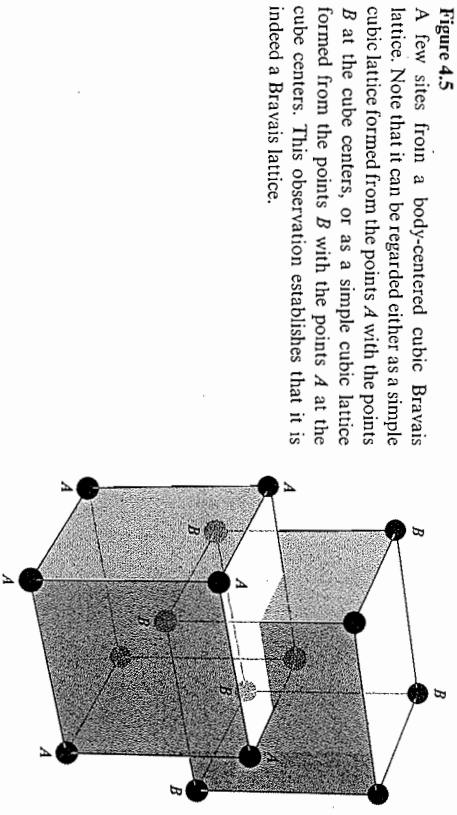
Figure 4.5
A few sites from a body-centered cubic Bravais lattice. Note that it can be regarded either as a simple cubic lattice formed from the points A with the points B at the cube centers, or as a simple cubic lattice formed from the points B with the points A at the cube centers. This observation 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)

$$a_1 = a\hat{x}, \quad a_2 = a\hat{y}, \quad a_3 = \frac{a}{2}(\hat{x} + \hat{y} + \hat{z}). \tag{4.3}$$

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 $P = -a_1 - a_2 + 2a_3$.
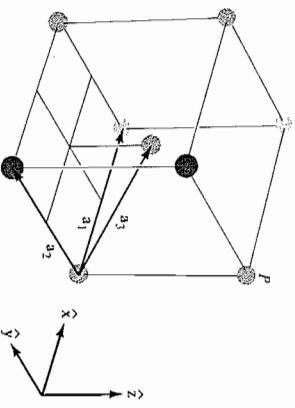
A more symmetric set (see Figure 4.7) is

$$a_1 = \frac{a}{2}(\hat{y} + \hat{z} - \hat{x}), \quad a_2 = \frac{a}{2}(\hat{z} + \hat{x} - \hat{y}), \quad a_3 = \frac{a}{2}(\hat{x} + \hat{y} - \hat{z}). \tag{4.4}$$

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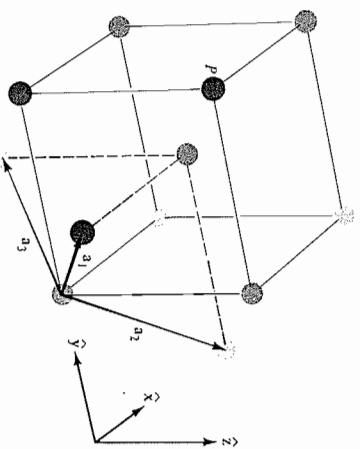

Figure 4.7
A more symmetric set of primitive vectors, specified in Eq. (4.4), for the body-centered cubic Bravais lattice. The point P, for example, has the form $P = 2a_1 + a_2 + a_3$.

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.
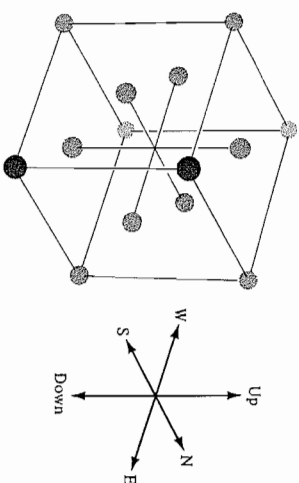
to the centers of all the horizontal faces. The original simple cubic lattice points are now centering points on the horizontal faces of the new simple cubic lattice, whereas the points that were added to the centers of the north-south faces of the original cubic lattice are in the centers of the east-west 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

$$a_1 = \frac{a}{2}(\hat{y} + \hat{z}), \quad a_2 = \frac{a}{2}(\hat{z} + \hat{x}), \quad a_3 = \frac{a}{2}(\hat{x} + \hat{y}). \tag{4.5}$$

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 $P = a_1 + a_2 + a_3$, $Q = 2a_2$, $R = a_2 + a_3$, and $S = -a_1 + a_2 + a_3$.
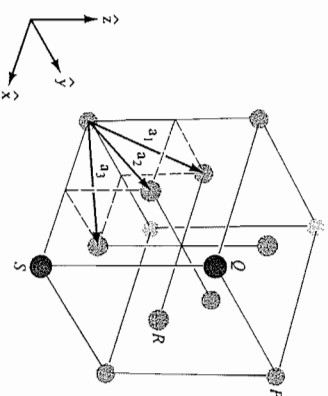
The face-centered cubic and body-centered cubic Bravais lattices are of great importance, since an enormous variety of solids crystallize in these forms with an atom (or ion) at each lattice site (see Tables 4.1 and 4.2). (The corresponding simple cubic form, however, is very rare, the alpha phase of 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 **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]

[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.
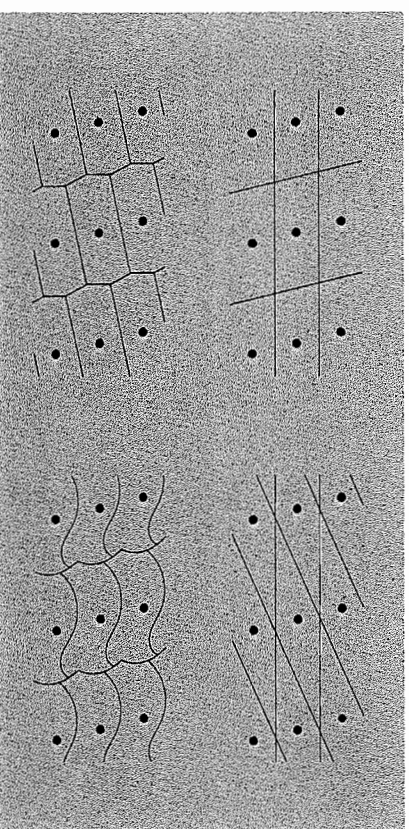

Figure 4.10
Several possible choices of primitive cell for a single two-dimensional Bravais lattice.

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 lattice[9] and v is the volume of the primitive cell, then $nv = 1$. Thus $v = 1/n$. Since v

[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.
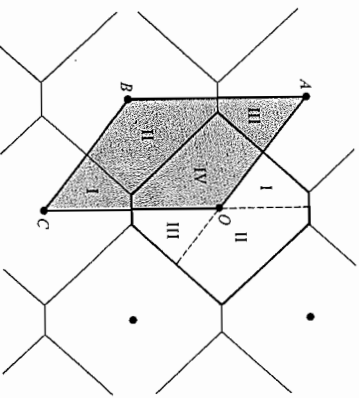
Figure 4.11
Two possible primitive cells for a two-dimensional Bravais lattice. The parallelogram cell (shaded) is obviously primitive; additional hexagonal cells are indicated to demonstrate that the hexagonal cell is also primitive. The parallelogram can be cut into pieces, which, when translated through appropriate 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

$$r = x_1 a_1 + x_2 a_2 + x_3 a_3 \qquad (4.6)$$

for all x_i ranging continuously between 0 and 1; i.e., the parallelepiped 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 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:
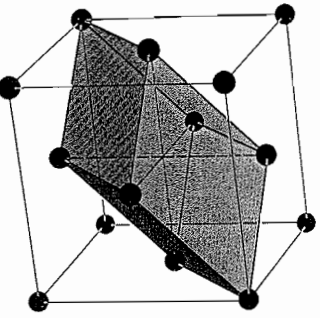
Figure 4.12
Primitive and conventional unit cells for the face-centered cubic Bravais lattice. The conventional cell is the large cube. The primitive cell is the figure with six parallelogram faces. It has one quarter the volume of the cube, and rather less symmetry.

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.
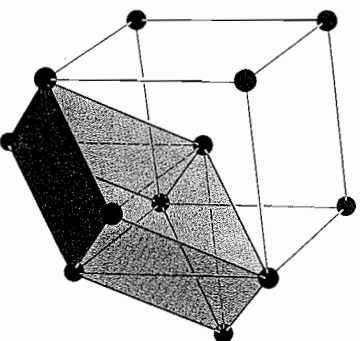
WIGNER-SEITZ PRIMITIVE CELL

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 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
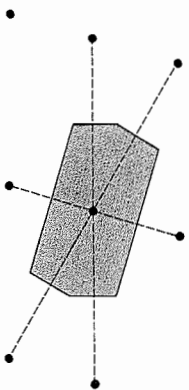

Figure 4.14
The Wigner-Seitz cell for a two-dimensional Bravais lattice. The six sides of the cell bisect the lines joining the central point to its six nearest neighboring points (shown as dashed lines). In two dimensions the Wigner-Seitz cell is always a hexagon unless the lattice is rectangular (see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

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

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).
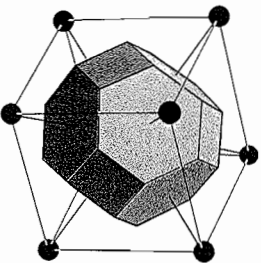

Figure 4.16
Wigner-Seitz cell for the face-centered cubic Bravais lattice (a "rhombic dodecahedron"). The surrounding cube is *not* the conventional cubic cell of Figure 4.12, but one in which lattice points are at the center of the cube and at the center of the 12 edges. Each of the 12 (congruent) faces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

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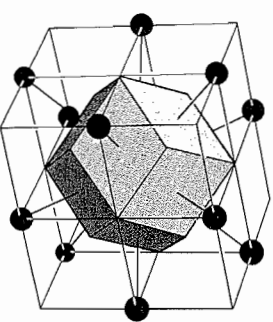
[12] A precise definition of "as symmetrical as" is given in Chapter 7.
[13] In practice only a fairly small number of nearby points actually yield planes that bound the cell.

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.
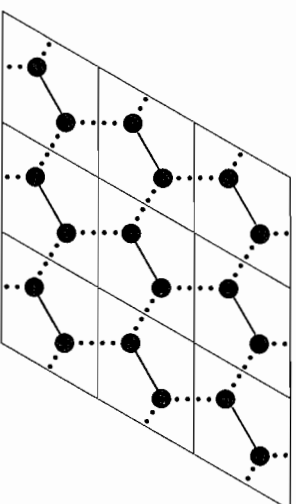

Figure 4.17
The honeycomb net, drawn so as to emphasize that it is a Bravais lattice with a two-point basis. The pairs of points joined by heavy solid lines are identically placed in the primitive cells (parallelograms) of the underlying Bravais lattice.

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

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

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[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 $\mathbf{0}$ and $(a/4)(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})$. The coordination number is 4 (Figure 4.18). The diamond lattice is not a Bravais lattice,

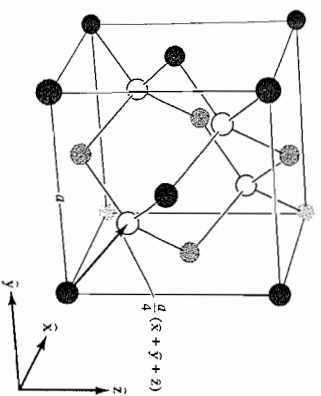$$\frac{a}{4}(\hat{x} + \hat{y} + \hat{z})$$

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
α-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
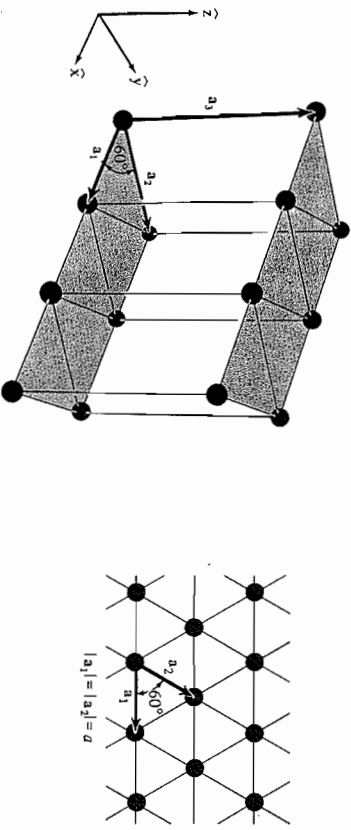

Figure 4.19
The simple hexagonal Bravais lattice. Two-dimensional triangular nets (shown in inset) are stacked directly above one another, a distance c apart.

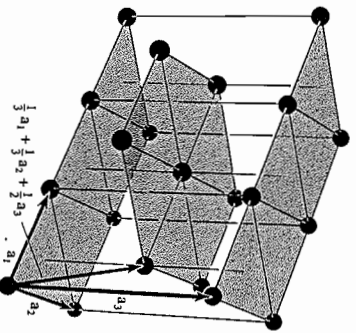$$|\mathbf{a}_1| = |\mathbf{a}_2| = a$$

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.

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):

$$c = \sqrt{\frac{8}{3}}\, a = 1.63299a. \qquad (4.10)$$

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.)
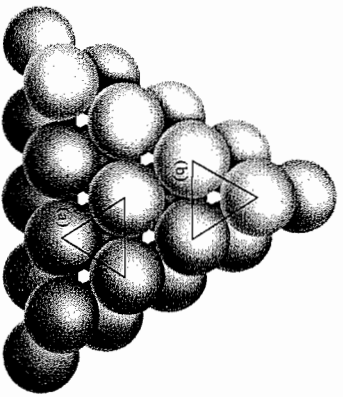
Because, however, the symmetry of the hexagonal close-packed lattice is independent of the c/a ratio, the name is not restricted to this case. The value $c/a = \sqrt{8/3}$ is sometimes called "ideal," and the truly close-packed structure, with the ideal value of c/a, is known as an ideal hcp structure. Unless, however, the physical units in the hcp structure are actually close-packed spheres, there is no reason 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).
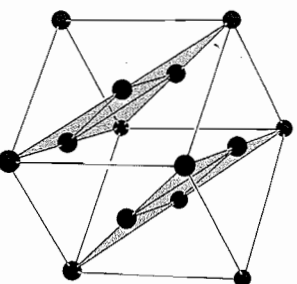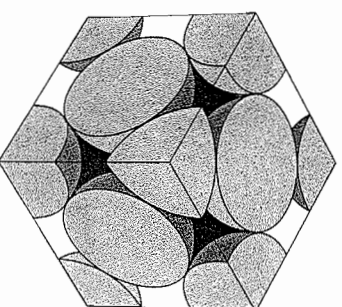
Figure 4.22
How to section the face-centered cubic Bravais lattice to get the layers pictured in Figure 4.21.

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. Certain 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 structure (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, $(a/2)(\hat{x} + \hat{y} + \hat{z})$.
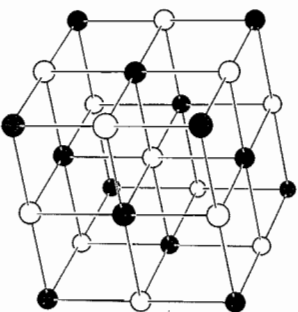

Figure 4.24
The sodium chloride structure. One type of ion is represented by black balls, the other type by white. The black and white balls form interpenetrating fcc lattices.

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

[17] For examples see Table 4.5.

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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.
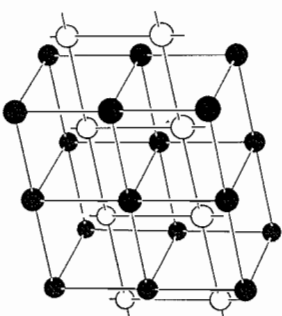

Table 4.6
SOME COMPOUNDS WITH THE CESIUM CHLORIDE STRUCTURE

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 examples see 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 such a 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:

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

7. Let N_n be the number of nth 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 nth 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 not on the line, 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 $\mathbf{k}$, 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

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

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

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

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

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

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

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

---

[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 vectors $\mathbf{R}$ 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 $\mathbf{b}_i$ satisfy[2]

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

where δ_{ij} is the Kronecker delta symbol:

$$\delta_{ij} = 0, \quad i \neq j;$$
$$\delta_{ij} = 1, \quad i = j. \tag{5.5}$$

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

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

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 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

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

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 noningegral 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

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

then

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

$$\mathbf{b}_1 = \frac{4\pi}{a}\frac{1}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}} - \hat{\mathbf{x}}), \quad \mathbf{b}_2 = \frac{4\pi}{a}\frac{1}{2}(\hat{\mathbf{z}} + \hat{\mathbf{x}} - \hat{\mathbf{y}}), \quad \mathbf{b}_3 = \frac{4\pi}{a}\frac{1}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}})$$ (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
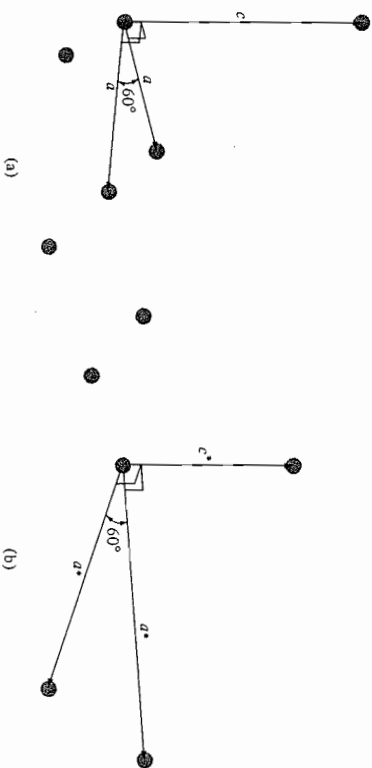
Figure 5.1
(a) Primitive vectors for the simple hexagonal Bravais lattice. (b) Primitive vectors for the lattice reciprocal to that generated by the primitive vectors in (a). The c and c^* axes are parallel. The a^* axes are rotated by 30° with respect to the a axes in the plane perpendicular to the 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 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.
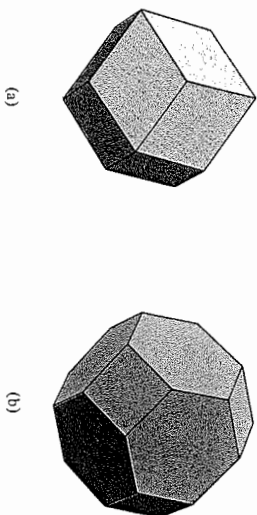
LATTICE PLANES

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.

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.
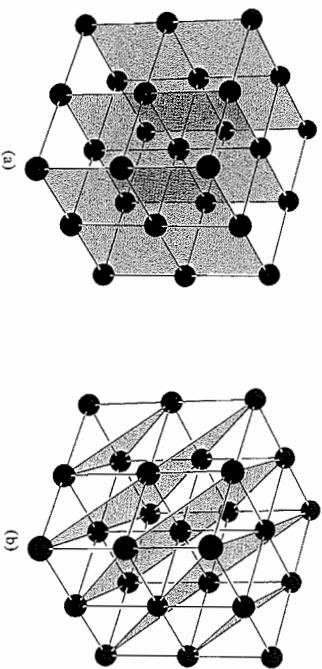

Figure 5.3
Some lattice planes (shaded) in a simple cubic Bravais lattice; (a) and (b) show two different ways of representing the lattice as a family of lattice planes.

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 nth 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.
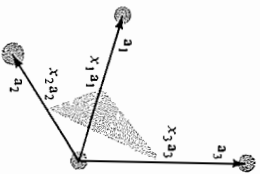
Figure 5.4
An illustration of the crystallographic definition of the Miller indices of a lattice plane. The shaded plane can be a portion of the continuous plane in which the points of the lattice plane lie, or any plane parallel to the lattice plane. The Miller indices are inversely proportional to 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 $[n_1 n_2 n_3]$ 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
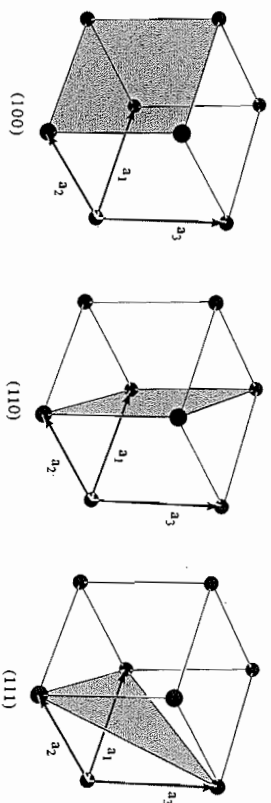
(100) (110) (111)

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 ⟨100⟩ 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 θ 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 θ^* 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 $\mathbf{K}_0$.)

6
Determination of Crystal Structures by X-ray Diffraction

Formulation of Bragg and von Laue

The Laue Condition and Ewald's Construction

Experimental Methods: Laue, Rotating Crystal, Powder

Geometrical Structure Factor

Atomic Form Factor

Typical interatomic distances in a solid are on the order of an angstrom (10^{-8} cm). An electromagnetic probe of the microscopic structure of a solid must therefore have a wavelength at least this short, corresponding to an energy of order

$$\hbar\omega = \frac{hc}{\lambda} = \frac{hc}{10^{-8}\ \text{cm}} \approx 12.3 \times 10^3\ \text{eV}. \qquad (6.1)$$

Energies like this, on the order of several thousands of electron volts (kilovolts or keV), are characteristic X-ray energies.

In this chapter we shall describe how the distribution of X rays scattered by a rigid,[1] periodic[2] array of ions reveals the locations of the ions within that structure. There are two equivalent ways to view the scattering of X rays by a perfect periodic structure, due to Bragg and to von Laue. Both viewpoints are still widely used. The von Laue approach, which exploits the reciprocal lattice, is closer to the spirit of modern solid state physics, but the Bragg approach is still in wide use by X-ray crystallographers. Both are described below, together with a proof of their equivalence.

BRAGG FORMULATION OF X-RAY DIFFRACTION BY A CRYSTAL

In 1913 W. H. and W. L. Bragg found that substances whose macroscopic forms were crystalline gave remarkably characteristic patterns of reflected X-radiation, quite unlike those produced by liquids. In crystalline materials, for certain sharply defined wavelengths and incident directions, intense peaks of scattered radiation (now known as Bragg peaks) were observed.

W. L. Bragg accounted for this by regarding a crystal as made out of parallel planes of ions, spaced a distance d apart (i.e., the lattice planes described in Chapter 5). The conditions for a sharp peak in the intensity of the scattered radiation were: (1) that the X rays should be specularly reflected[3] by the ions in any one plane and (2) that the reflected rays from successive planes should interfere constructively. Rays specularly reflected from adjoining planes are shown in Figure 6.1. The path difference between the two rays is just $2d \sin\theta$, where θ is the angle of incidence.[4] For the rays to interfere constructively, this path difference must be an integral number of wavelengths, leading to the celebrated Bragg condition:

$$n\lambda = 2d \sin\theta. \qquad (6.2)$$

The integer n is known as the order of the corresponding reflection. For a beam of X rays containing a range of different wavelengths ("white radiation") many different reflections are observed. Not only can one have higher-order reflections from a given set of lattice planes, but in addition one must recognize that there are

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[1] Actually the ions vibrate about their ideal equilibrium sites (Chapters 21–26). This does not affect the conclusions reached in this chapter (though in the early days of X-ray diffraction it was not clear why such vibrations did not obliterate the pattern characteristic of a periodic structure). It turns out that the vibrations have two main consequences (see Appendix N): (a) the intensity in the characteristic peaks that reveal the crystal structure is diminished, but not eliminated; and (b) a much weaker continuous background of radiation (the "diffuse background") is produced.

[2] Amorphous solids and liquids have about the same density as crystalline solids, and are therefore also susceptible to probing with X rays. However, the discrete, sharp peaks of scattered radiation characteristic of crystals are not found.

[3] In specular reflection the angle of incidence equals the angle of reflection.

[4] The angle of incidence in X-ray crystallography is conventionally measured from the plane of reflection rather than from the normal to that plane (as in classical optics). Note that θ is just half the angle of deflection of the incident beam (Figure 6.2).

Figure 6.1
A Bragg reflection from a particular family of lattice planes, separated by a distance d. Incident and reflected rays are shown for the two neighboring planes. The path difference is $2d \sin\theta$.
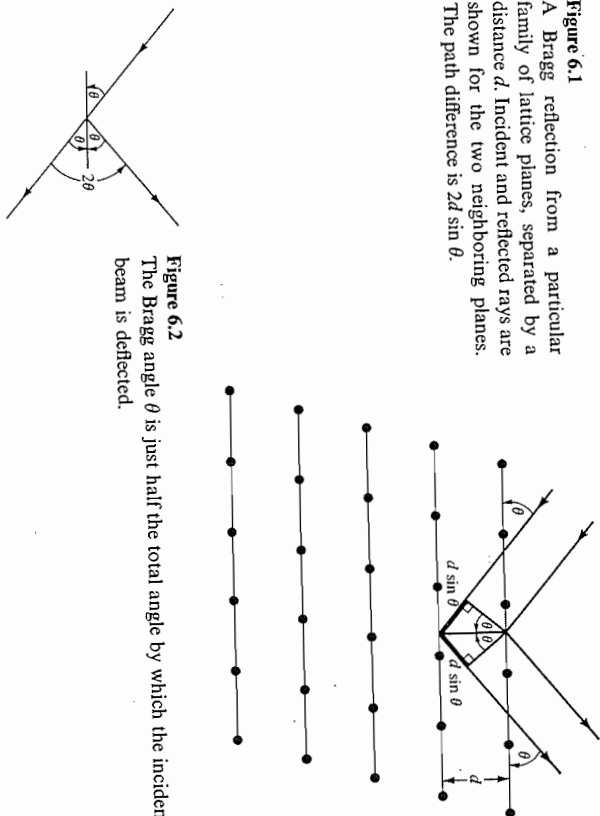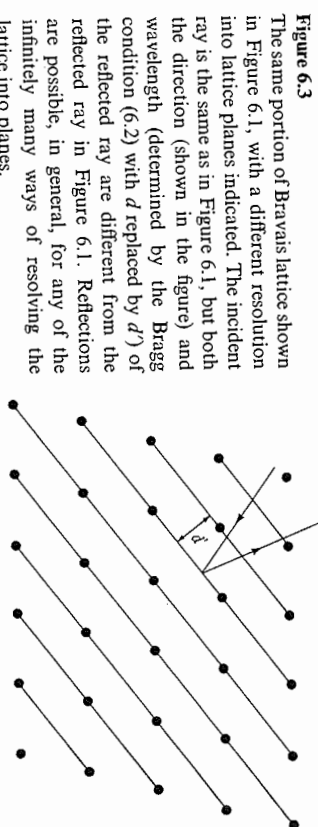

Figure 6.2
The Bragg angle θ is just half the total angle by which the incident beam is deflected.

Figure 6.3
The same portion of Bravais lattice shown in Figure 6.1, with a different resolution into lattice planes indicated. The incident ray is the same as in Figure 6.1, but both the direction (shown in the figure) and wavelength (determined by the Bragg condition (6.2) with d replaced by d') of the reflected ray in Figure 6.1. Reflections are possible, in general, for any of the infinitely many ways of resolving the lattice into planes.

many different ways of sectioning the crystal into planes, each of which will itself produce further reflections (see, for example, Figure 5.3 or Figure 6.3).

VON LAUE FORMULATION OF X-RAY DIFFRACTION BY A CRYSTAL

The von Laue approach differs from the Bragg approach in that no particular sectioning of the crystal into lattice planes is singled out, and no *ad hoc* assumption of specular reflection is imposed.[5] Instead one regards the crystal as composed of

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[5] The Bragg assumption of specular reflection is, however, equivalent to the assumption that rays scattered from individual ions within each lattice plane interfere constructively. Thus both the Bragg and the von Laue approaches are based on the same physical assumptions, and their precise equivalence (see page 99) is to be expected.
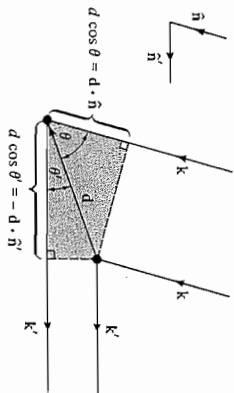
Figure 6.4

Illustrating that the path difference for rays scattered from two points separated by **d** is given by Eq. (6.3) or (6.4).

$d \cos\theta = \mathbf{d} \cdot \hat{\mathbf{n}}$

$d \cos\theta = -\mathbf{d} \cdot \hat{\mathbf{n}}'$

identical microscopic objects (sets of ions or atoms) placed at the sites **R** of a Bravais lattice, each of which can reradiate the incident radiation in all directions. Sharp peaks will be observed only in directions and at wavelengths for which the rays scattered from all lattice points interfere constructively.

To find the condition for constructive interference, consider first just two scatterers, separated by a displacement vector **d** (Figure 6.4). Let an X ray be incident from very far away, along a direction $\hat{\mathbf{n}}$, with wavelength λ, and wave vector $\mathbf{k} = 2\pi\hat{\mathbf{n}}/\lambda$. A scattered ray will be observed in a direction $\hat{\mathbf{n}}'$ with wavelength[6] λ and wave vector $\mathbf{k}' = 2\pi\hat{\mathbf{n}}'/\lambda$, provided that the path difference between the rays scattered by each of the two ions is an integral number of wavelengths. From Figure 6.4 it can be seen that this path difference is just

$$d \cos\theta + d \cos\theta' = \mathbf{d} \cdot (\hat{\mathbf{n}} - \hat{\mathbf{n}}').$$ (6.3)

The condition for constructive interference is thus

$$\mathbf{d} \cdot (\hat{\mathbf{n}} - \hat{\mathbf{n}}') = m\lambda,$$ (6.4)

for integral m. Multiplying both sides of (6.4) by $2\pi/\lambda$ yields a condition on the incident and scattered wave vectors:

$$\mathbf{d} \cdot (\mathbf{k} - \mathbf{k}') = 2\pi m,$$ (6.5)

for integral m.

Next, we consider not just two scatterers, but an array of scatterers, at the sites of a Bravais lattice. Since the lattice sites are displaced from one another by the Bravais lattice vectors **R**, the condition that all scattered rays interfere constructively is that condition (6.5) hold simultaneously for all values of **d** that are Bravais lattice vectors:

$$\mathbf{R} \cdot (\mathbf{k} - \mathbf{k}') = 2\pi m, \qquad \begin{array}{l} \text{for integral } m \text{ and} \\ \text{all Bravais lattice} \\ \text{vectors } \mathbf{R}. \end{array}$$ (6.6)

This can be written in the equivalent form

$$e^{i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{R}} = 1, \quad \text{for all Bravais lattice vectors } \mathbf{R}.$$ (6.7)

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[6] Here (and in the Bragg picture) we assume that the incident and scattered radiation has the same wavelength. In terms of photons this means that no energy has been lost in the scattering, i.e., that the scattering is elastic. To a good approximation the bulk of the scattered radiation is elastically scattered, though there is much to be learned from the study of that small component of the radiation that is inelastically scattered (Chapter 24 and Appendix N).

Comparing this condition with the definition (5.2) of the reciprocal lattice, we arrive at the Laue condition that *constructive interference will occur provided that the change in wave vector, $\mathbf{K} = \mathbf{k}' - \mathbf{k}$, is a vector of the reciprocal lattice.*

It is sometimes convenient to have an alternative formulation of the Laue condition, stated entirely in terms of the incident wave vector **k**. First note that because the reciprocal lattice is a Bravais lattice, if $\mathbf{k}' - \mathbf{k}$ is a reciprocal lattice vector, so is $\mathbf{k} - \mathbf{k}'$. Calling the latter vector **K**, the condition that **k** and **k**' have the same magnitude is

$$k = |\mathbf{k} - \mathbf{K}|.$$ (6.8)

Squaring both sides of (6.8) yields the condition

$$\mathbf{k} \cdot \hat{\mathbf{K}} = \tfrac{1}{2}K;$$ (6.9)

i.e., the component of the incident wave vector **k** along the reciprocal lattice vector **K** must be half the length of **K**.

Thus an incident wave vector **k** will satisfy the Laue condition if and only if the tip of the vector lies in a plane that is the perpendicular bisector of a line joining the origin of k-space to a reciprocal lattice point **K** (Figure 6.5). Such k-space planes are called *Bragg planes*.

Figure 6.5

The Laue condition. If the sum of **k** and $-\mathbf{k}'$ is a vector **K**, and if **k** and **k**' have the same length, then the tip of the vector **k** is equidistant from the origin O and the tip of the vector **K**, and therefore it lies in the plane bisecting the line joining the origin to the tip of **K**.
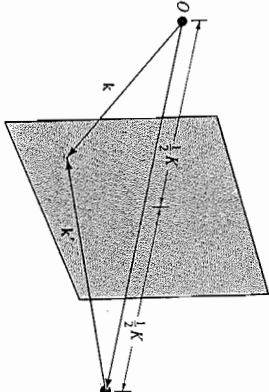
It is a consequence of the equivalence of the Bragg and von Laue points of view, demonstrated in the following section, that the k-space Bragg plane associated with a particular diffraction peak in the Laue formulation is parallel to the family of direct lattice planes responsible for the peak in the Bragg formulation.

EQUIVALENCE OF THE BRAGG AND VON LAUE FORMULATIONS

The equivalence of these two criteria for constructive interference of X rays by a crystal follows from the relation between vectors of the reciprocal lattice and families of direct lattice planes (see Chapter 5). Suppose the incident and scattered wave vectors, **k** and **k**', satisfy the Laue condition that $\mathbf{K} = \mathbf{k}' - \mathbf{k}$ be a reciprocal lattice vector. Because the incident and scattered waves have the same wavelength,[6] **k**' and **k** have the same magnitudes. It follows (see Figure 6.6) that **k**' and **k** make the same angle θ with the plane perpendicular to **K**. Therefore the scattering can be viewed as a Bragg reflection, with Bragg angle θ, from the family of direct lattice planes perpendicular to the reciprocal lattice vector **K**.
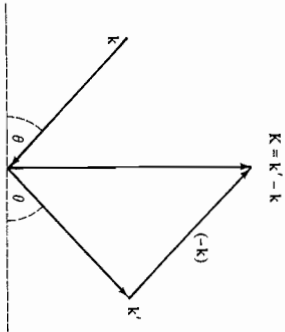
Figure 6.6
The plane of the paper contains the incident wave vector $\mathbf{k}$, the reflected wave vector $\mathbf{k}'$, and their difference $\mathbf{K}$ satisfying the Laue condition. Since the scattering is elastic ($k' = k$), the direction of $\mathbf{K}$ bisects the angle between $\mathbf{k}$ and $\mathbf{k}'$. The dashed line is the intersection of the plane perpendicular to $\mathbf{K}$ with the plane of the paper.

To demonstrate that this reflection satisfies the Bragg condition (6.2), note that the vector $\mathbf{K}$ is an integral multiple[7] of the shortest reciprocal lattice vector $\mathbf{K}_0$ parallel to $\mathbf{K}$. According to the theorem on page 90, the magnitude of $\mathbf{K}_0$ is just $2\pi/d$, where d is the distance between successive planes in the family perpendicular to $\mathbf{K}$. Thus

$$K = \frac{2\pi n}{d}.$$ (6.10)

On the other hand, it follows from Figure 6.6 that $K = 2k \sin\theta$, and thus

$$k \sin\theta = \frac{\pi n}{d}.$$ (6.11)

Since $k = 2\pi/\lambda$, Eq. (6.11) implies that the wavelength satisfies the Bragg condition (6.2).

Thus *a Laue diffraction peak corresponding to a change in wave vector given by the reciprocal lattice vector* $\mathbf{K}$ *corresponds to a Bragg reflection from the family of direct lattice planes perpendicular to* $\mathbf{K}$. *The order,* n, *of the Bragg reflection is just the length of* $\mathbf{K}$ *divided by the length of the shortest reciprocal lattice vector parallel to* $\mathbf{K}$.

Since the reciprocal lattice associated with a given Bravais lattice is far more easily visualized than the set of all possible planes into which the Bravais lattice can be resolved, the Laue condition for diffraction peaks is far more simple to work with than the Bragg condition. In the rest of this chapter we shall apply the Laue condition to a description of three of the most important ways in which X-ray crystallographic analyses of real samples are performed, and to a discussion of how one can extract information not only about the underlying Bravais lattice, but also about the arrangement of ions within the primitive cell.

EXPERIMENTAL GEOMETRIES SUGGESTED BY THE LAUE CONDITION

An incident wave vector $\mathbf{k}$ will lead to a diffraction peak (or "Bragg reflection") if and only if the tip of the wave vector lies on a k-space Bragg plane. Since the set of all

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[7] This is an elementary consequence of the fact that the reciprocal lattice is a Bravais lattice. See Chapter 5, Problem 4.

Bragg planes is a discrete family of planes, it cannot begin to fill up three-dimensional k-space, and in general the tip of $\mathbf{k}$ will not lie on a Bragg plane. Thus for a fixed incident wave vector—i.e., for a fixed X-ray wavelength and fixed incident direction relative to the crystal axes—there will be in general no diffraction peaks at all.
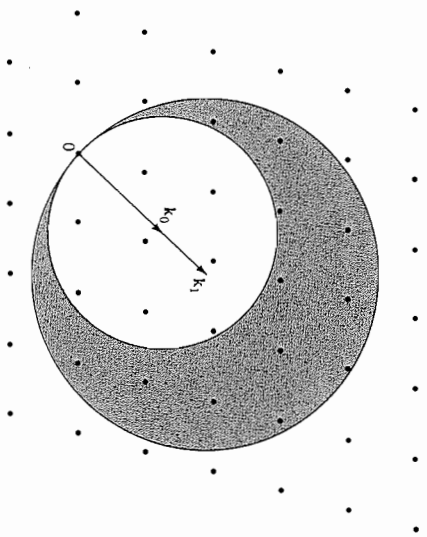
If one wishes to search experimentally for Bragg peaks one must therefore relax the constraint of fixed $\mathbf{k}$, either varying the magnitude of $\mathbf{k}$ (i.e., varying the wavelength of the incident beam) or varying its direction (in practice, varying the orientation of the crystal with respect to the incident direction).

The Ewald Construction

A simple geometric construction due to Ewald is of great help in visualizing these various methods and in deducing the crystal structure from the peaks so observed. We draw in k-space a sphere centered on the tip of the incident wave vector $\mathbf{k}$ of radius k (so that it passes through the origin). Evidently (see Figure 6.7) there will be *some* wave vector $\mathbf{k}'$ satisfying the Laue condition if and only if some reciprocal lattice point (in addition to the origin) lies on the surface of the sphere, in which case there will be a Bragg reflection from the family of direct lattice planes perpendicular to that reciprocal lattice vector.

Figure 6.7
The Ewald construction. Given the incident wave vector $\mathbf{k}$, a sphere of radius k is drawn about the point $\mathbf{k}$. Diffraction peaks corresponding to reciprocal lattice vectors $\mathbf{K}$ will be observed only if $\mathbf{K}$ gives a reciprocal lattice point on the surface of the sphere. Such a reciprocal lattice vector is indicated in the figure, together with the wave vector $\mathbf{k}'$ of the Bragg reflected ray.
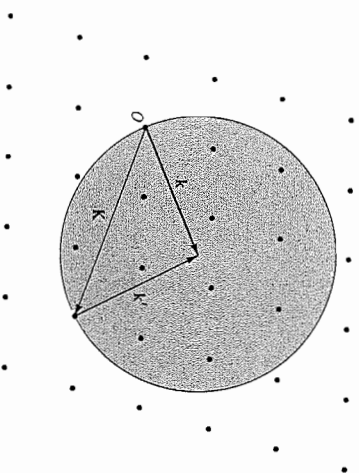
In general, a sphere in k-space with the origin on its surface will have no other reciprocal lattice points on its surface, and therefore the Ewald construction confirms our observation that for a general incident wave vector there will be no Bragg peaks. One can, however, ensure that some Bragg peaks will be produced by several techniques:

1. **The Laue Method**   One can continue to scatter from a single crystal of fixed orientation from a fixed incident direction $\hat{\mathbf{n}}$, but can search for Bragg peaks by using not a monochromatic X-ray beam, but one containing wavelengths from λ_1 up to λ_0. The Ewald sphere will then expand into the region contained between the two spheres determined by $k_0 = 2\pi\hat{\mathbf{n}}/\lambda_0$ and $k_1 = 2\pi\hat{\mathbf{n}}/\lambda_1$, and Bragg peaks will be observed corresponding to any reciprocal lattice vectors lying within this region (Figure 6.8). By making the spread in wavelengths sufficiently large, one

can be sure of finding some reciprocal lattice points within the region; whereas by keeping it from getting too large, one can avoid too many Bragg reflections, thereby keeping the picture fairly simple.

The Laue method is probably best suited for determining the orientation of a single crystal specimen whose structure is known, since, for example, if the incident direction lies along a symmetry axis of the crystal, the pattern of spots produced by the Bragg reflected rays will have the same symmetry. Since solid state physicists generally do study substances of known crystal structure, the Laue method is probably the one of greatest practical interest.

2. **The Rotating-Crystal Method**   This method uses monochromatic X rays, but allows the angle of incidence to vary. In practice the direction of the X-ray beam is kept fixed, and the orientation of the crystal varied instead. In the rotating crystal method the crystal is rotated about some fixed axis, and all Bragg peaks that occur during the rotation are recorded on a film. As the crystal rotates, the reciprocal lattice it determines will rotate by the same amount about the same axis. Thus the Ewald sphere (which is determined by the fixed incident wave vector **k**) is fixed in *k*-space, while the entire reciprocal lattice rotates about the axis of rotation of the crystal. During this rotation each reciprocal lattice point traverses a circle about the rotation axis, and a Bragg reflection occurs whenever this circle intersects the Ewald sphere. This is illustrated in Figure 6.9 for a particularly simple geometry.

3. **The Powder or Debye-Scherrer Method**   This is equivalent to a rotating crystal experiment in which, in addition, the axis of rotation is varied over all possible orientations. In practice this isotropic averaging of the incident direction is

Figure 6.8
The Ewald construction for the Laue method. The crystal and incident X-ray direction are fixed, and a continuous range of wavelengths, corresponding to wave vectors between k_0 and k_1 in magnitude, is present. The Ewald spheres for all incident wave vectors fill the shaded region between the sphere centered on the tip of the vector k_0 and that centered on the tip of k_1. Bragg peaks will be observed corresponding to all reciprocal lattice points lying within the shaded region. (For simplicity in illustration, the incident direction has been taken to lie in a lattice plane, and only reciprocal lattice points lying in that plane are shown.)

achieved by using a polycrystalline sample or a powder, grains of which are still enormous on the atomic scale and therefore capable of diffracting X rays. Because the crystal axes of the individual grains are randomly oriented, the diffraction pattern produced by such a powder is what one would produce by combining the diffraction patterns for all possible orientations of a single crystal.

The Bragg reflections are now determined by fixing the incident **k** vector, and with it the Ewald sphere, and allowing the reciprocal lattice to rotate through all possible angles about the origin, so that each reciprocal lattice vector **K** generates a sphere of radius K about the origin. Such a sphere will intersect the Ewald sphere in a circle (Figure 6.10a) provided that K is less than $2k$. The vector joining any point on such a circle with the tip of the incident vector **k** is a wave vector **k'** for which scattered radiation will be observed. Thus each reciprocal lattice vector of length less than $2k$ generates a cone of scattered radiation at an angle ϕ to the forward direction, where (Figure 6.10b)

$$K = 2k \sin \tfrac{1}{2}\phi. \qquad (6.12)$$

Figure 6.9
The Ewald construction for the rotating-crystal method. For simplicity a case is shown in which the incident wave vector lies in a lattice plane, and the axis of rotation is perpendicular to that plane. The concentric circles are the orbits swept out under the rotation by the reciprocal lattice vectors lying in the plane perpendicular to the axis containing **k**. Each intersection of such a circle with the Ewald sphere gives the wave vector of a Bragg reflected ray. (Additional Bragg reflected wave vectors associated with reciprocal lattice vectors in other planes are not shown.)
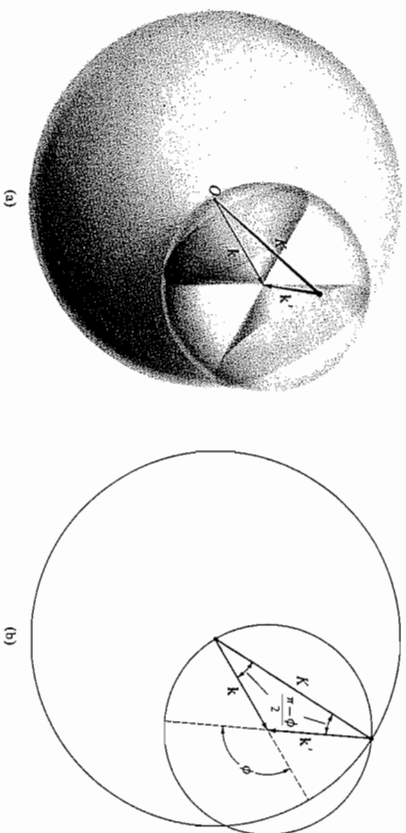
(a)

(b)

Figure 6.10

The Ewald construction for the powder method. (a) The Ewald sphere is the smaller sphere. It is centered on the tip of the incident wave vector $\mathbf{k}$ with radius k, so that the origin O is on its surface. The larger sphere is centered on the origin and has a radius K. The two spheres intersect in a circle (foreshortened to an ellipse). Bragg reflections will occur for any wave vector $\mathbf{k}'$ connecting any point on the circle of intersection to the tip of the vector $\mathbf{k}$. The scattered rays therefore lie on the cone that opens in the direction opposite to $\mathbf{k}$. (b) A plane section of (a), containing the incident wave vector. The triangle is isosceles, and thus $K = 2k \sin \frac{1}{2}\phi$.

By measuring the angles ϕ at which Bragg reflections are observed, one therefore learns the lengths of all reciprocal lattice vectors shorter than $2k$. Armed with this information, some facts about the macroscopic crystal symmetry, and the fact that the reciprocal lattice is a Bravais lattice, one can usually construct the reciprocal lattice itself (see, for example, Problem 1).

DIFFRACTION BY A MONATOMIC LATTICE WITH A BASIS; THE GEOMETRICAL STRUCTURE FACTOR

The preceding discussion was based on the condition (6.7) that rays scattered from each primitive cell should interfere constructively. If the crystal structure is that of a monatomic lattice with an n-atom basis (for example, carbon in the diamond structure or hexagonal close-packed beryllium, both of which have $n = 2$), then the contents of each primitive cell can be further analyzed into a set of identical scatterers at positions $\mathbf{d}_1, \ldots, \mathbf{d}_n$ within the cell. The intensity of radiation in a given Bragg peak will depend on the extent to which the rays scattered from these basis sites interfere with one another, being greatest when there is complete constructive interference and vanishing altogether should there happen to be complete destructive interference.

If the Bragg peak is associated with a change in wave vector $\mathbf{k}' - \mathbf{k} = \mathbf{K}$, then the path difference (Figure 6.4) between the rays scattered at $\mathbf{d}_i$ and $\mathbf{d}_j$ will be $\mathbf{K} \cdot (\mathbf{d}_i - \mathbf{d}_j)$ and the phases of the two rays will differ by a factor $e^{i\mathbf{K} \cdot (\mathbf{d}_i - \mathbf{d}_j)}$. Thus the phases of the rays scattered at $\mathbf{d}_1, \ldots, \mathbf{d}_n$ are in the ratios $e^{i\mathbf{K} \cdot \mathbf{d}_1}, \ldots, e^{i\mathbf{K} \cdot \mathbf{d}_n}$. The net ray scattered by

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the entire primitive cell is the sum of the individual rays, and will therefore have an amplitude containing the factor

$$S_\mathbf{K} = \sum_{j=1}^{n} e^{i\mathbf{K} \cdot \mathbf{d}_j}. \tag{6.13}$$

The quantity $S_\mathbf{K}$, known as the *geometrical structure factor*, expresses the extent to which interference of the waves scattered from identical ions within the basis can diminish the intensity of the Bragg peak associated with the reciprocal lattice vector $\mathbf{K}$. The intensity in the Bragg peak, being proportional to the square of the absolute value of the amplitude, will contain a factor $|S_\mathbf{K}|^2$. It is important to note that this is not the only source of $\mathbf{K}$ dependence to the intensity. Further dependence on the change in wave vector comes both from the ordinary angular dependence of any electromagnetic scattering, together with the influence on the scattering of the detailed internal structure of each individual ion in the basis. Therefore the structure factor alone cannot be used to predict the absolute intensity in a Bragg peak.[8] It can, however, lead to a characteristic dependence on $\mathbf{K}$ that is easily discerned even though other less distinctive $\mathbf{K}$ dependences have been superimposed upon it. The one case, in which the structure factor can be used with assurance is when it vanishes. This occurs when the elements of the basis are so arranged that there is complete destructive interference for the $\mathbf{K}$ in question; in that case no features of the rays scattered by the individual basis elements can prevent the net ray from vanishing.

We illustrate the importance of a vanishing structure factor in two cases[9]:

1. *Body-Centered Cubic Considered as Simple Cubic with a Basis* Since the body-centered cubic lattice is a Bravais lattice, we know that Bragg reflections will occur when the change in wave vector $\mathbf{K}$ is a vector of the reciprocal lattice, which is face-centered cubic. Sometimes, however, it is convenient to regard the bcc lattice as a simple cubic lattice generated by primitive vectors $a\hat{x}$, $a\hat{y}$, and $a\hat{z}$, with a two-point basis consisting of $\mathbf{d}_1 = 0$ and $\mathbf{d}_2 = (a/2)(\hat{x} + \hat{y} + \hat{z})$. From this point of view, there reciprocal lattice is also simple cubic, with a cubic cell of side $2\pi/a$. However, there will now be a structure factor $S_\mathbf{K}$ associated with each Bragg reflection. In the present case, (6.13) gives

$$S_\mathbf{K} = 1 + \exp \left[i\mathbf{K} \cdot \tfrac{1}{2}a(\hat{x} + \hat{y} + \hat{z}) \right]. \tag{6.14}$$

A general vector in the simple cubic reciprocal lattice has the form

$$\mathbf{K} = \frac{2\pi}{a}(n_1\hat{x} + n_2\hat{y} + n_3\hat{z}). \tag{6.15}$$

Substituting this into (6.14), we find a structure factor

$$S_\mathbf{K} = 1 + e^{i\pi(n_1+n_2+n_3)} = 1 + (-1)^{n_1+n_2+n_3}$$
$$= \begin{cases} 2, & n_1 + n_2 + n_3 \quad \text{even,} \\ 0, & n_1 + n_2 + n_3 \quad \text{odd.} \end{cases} \tag{6.16}$$

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[8] A brief but thorough discussion of the scattering of electromagnetic radiation by crystals, including the derivation of detailed intensity formulas for the various experimental geometries described above, is given by Landau and Lifshitz, *Electrodynamics of Continuous Media*, Chapter 15, , Addison-Wesley, Reading, Mass., 1966.

[9] Further examples are given in Problems 2 and 3.

Thus those points in the simple cubic reciprocal lattice, the sum of whose coordinates with respect to the cubic primitive vectors are odd, will actually have no Bragg reflection associated with them. This converts the simple cubic reciprocal lattice into the face-centered cubic direct lattice structure that we would have had if we had treated the body-centered cubic direct lattice as a Bravais lattice rather than as a lattice with a basis (see Figure 6.11).
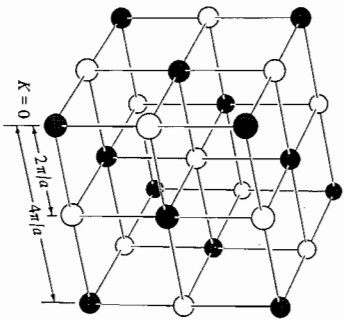
Figure 6.11
Points in the simple cubic reciprocal lattice of side $2\pi/a$, for which the structure factor (6.16) vanishes, are those (white circles) that can be reached from the origin by moving along an odd number of nearest-neighbor bonds. When such sites are eliminated, the remaining sites (black circles) constitute a face-centered cubic lattice with cubic cell of side $4\pi/a$.

Thus if, either inadvertently or for reasons of greater symmetry in description, one chooses to describe a Bravais lattice as a lattice with a basis, one still recovers the correct description of X-ray diffraction, provided that the vanishing of the structure factor is taken into account.

2. *Monatomic Diamond Lattice*   The monatomic diamond lattice (carbon, silicon, germanium, or grey tin) is not a Bravais lattice and must be described as a lattice with a basis. The underlying Bravais lattice is face-centered cubic, and the basis can be taken to be $\mathbf{d}_1 = 0$, $\mathbf{d}_2 = (a/4)(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})$, where $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, and $\hat{\mathbf{z}}$ are along the cubic axes and a is the side of the conventional cubic cell. The reciprocal lattice is body-centered cubic with conventional cubic cell of side $4\pi/a$. If we take as primitive vectors

$$\mathbf{b}_1 = \frac{2\pi}{a}(\hat{\mathbf{y}} + \hat{\mathbf{z}} - \hat{\mathbf{x}}), \quad \mathbf{b}_2 = \frac{2\pi}{a}(\hat{\mathbf{z}} + \hat{\mathbf{x}} - \hat{\mathbf{y}}), \quad \mathbf{b}_3 = \frac{2\pi}{a}(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}}), \quad (6.17)$$

then the structure factor (6.13) for $\mathbf{K} = \Sigma n_i \mathbf{b}_i$ is

$$S_\mathbf{K} = 1 + \exp\left[\tfrac{1}{2}i\pi(n_1 + n_2 + n_3)\right]$$
$$= \begin{cases} 2, & n_1 + n_2 + n_3 \text{ twice an even number,} \\ 1 \pm i, & n_1 + n_2 + n_3 \text{ odd,} \\ 0, & n_1 + n_2 + n_3 \text{ twice an odd number.} \end{cases} \quad (6.18)$$

To interpret these conditions on Σn_i geometrically, note that if we substitute (6.17) into $\mathbf{K} = \Sigma n_i \mathbf{b}_i$, we can write the general reciprocal lattice vector in the form

$$\mathbf{K} = \frac{4\pi}{a}(v_1\hat{\mathbf{x}} + v_2\hat{\mathbf{y}} + v_3\hat{\mathbf{z}}), \quad (6.19)$$

where

$$v_j = \tfrac{1}{2}(n_1 + n_2 + n_3) - n_j, \quad \sum_{j=1}^{3} v_j = \tfrac{1}{2}(n_1 + n_2 + n_3). \quad (6.20)$$

We know (see Chapter 5) that the reciprocal to the fcc lattice with cubic cell of side a is a bcc lattice with cubic cell of side $4\pi/a$. Let us regard this as composed of two simple cubic lattices of side $4\pi/a$. The first, containing the origin ($\mathbf{K} = 0$), must have all v_i integers (according to (6.19)). The second, containing the "body-centered point" $(4\pi/a)\tfrac{1}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})$, must therefore have all v_i integers $+ \tfrac{1}{2}$ (according to (6.20)).

Comparing this with (6.18), we find that the points with structure factor $1 \pm i$ are those in the simple cubic sublattice of "body-centered" points. Those whose structure factor S is 2 or 0 are in the simple cubic sublattice containing the origin, where Σv_i is even when $S = 2$ and odd when $S = 0$. Thus the points with zero structure factor are again removed by applying the construction illustrated in Figure 6.11 to the simple cubic sublattice containing the origin, converting it to a face-centered cubic structure (Figure 6.12).
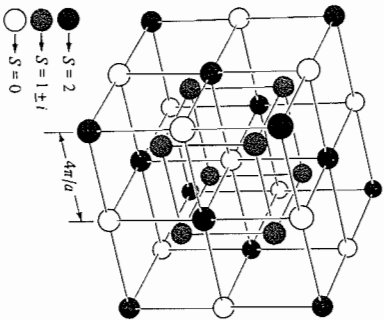
Figure 6.12
The body-centered cubic lattice with cubic cell side $4\pi/a$ that is reciprocal to a face-centered cubic lattice with cubic cell side a. When the fcc lattice is that underlying the diamond structure, then the white circles indicate sites with zero structure factor. (The black circles are sites with structure factor 2, and the gray ones are sites with structure factor $1 \pm i$.)

● → S = 2
◐ → S = 1 ± i
○ → S = 0

DIFFRACTION BY A POLYATOMIC CRYSTAL; THE ATOMIC FORM FACTOR

If the ions in the basis are not identical, the structure factor (6.13) assumes the form

$$S_\mathbf{K} = \sum_{j=1}^{n} f_j(\mathbf{K})e^{i\mathbf{K}\cdot\mathbf{d}_j}, \quad (6.21)$$

where f_j, known as the *atomic form factor*, is entirely determined by the internal structure of the ion that occupies position $\mathbf{d}_j$ in the basis. Identical ions have identical form factors (regardless of where they are placed), so (6.21) reduces back to (6.13), multiplied by the common value of the form factors, in the monatomic case.

In elementary treatments the atomic form factor associated with a Bragg reflection

given by the reciprocal lattice vector $\mathbf{K}$ is taken to be proportional to the Fourier transform of the electronic charge distribution of the corresponding ion[10]:

$$f_j(\mathbf{K}) = -\frac{1}{e} \int d\mathbf{r}\, e^{i\mathbf{K}\cdot\mathbf{r}}\, \rho_j(\mathbf{r}). \qquad (6.22)$$

Thus the atomic form factor f_j depends on $\mathbf{K}$ and on the detailed features of the charge distribution of the ion that occupies position $\mathbf{d}_j$ in the basis. As a result, one would not expect the structure factor to vanish for any $\mathbf{K}$ unless there is some fortuitous relation between form factors of different types. By making reasonable assumptions about the $\mathbf{K}$ dependence of the different form factors, one can often distinguish quite conclusively between various possible crystal structures on the basis of the variation with $\mathbf{K}$ of the Bragg peak intensities (see, for example, Problem 5).

This concludes our discussion of the Bragg reflection of X rays. Our analysis has exploited no properties of the X rays other than their wave nature.[11] Consequently we shall find many of the concepts and results of this chapter reappearing in subsequent discussions of other wave phenomena in solids, such as electrons (Chapter 9) and neutrons (Chapter 24).[12]

PROBLEMS

1. Powder specimens of three different monatomic cubic crystals are analyzed with a Debye-Scherrer camera. It is known that one sample is face-centered cubic, one is body-centered cubic, and one has the diamond structure. The approximate positions of the first four diffraction rings in each case are (see Figure 6.13):

VALUES OF ϕ FOR SAMPLES

A	B	C
42.2°	28.8°	42.8°
49.2	41.0	73.2
72.0	50.8	89.0
87.3	59.6	115.0

(a) Identify the crystal structures of A, B, and C.

(b) If the wavelength of the incident X-ray beam is 1.5 Å, what is the length of the side of the conventional cubic cell in each case?

(c) If the diamond structure were replaced by a zincblende structure with a cubic unit cell of the same side, at what angles would the first four rings now occur?

[10] The electronic charge density $\rho_j(\mathbf{r})$ is that of an ion of type j placed at $\mathbf{r} = 0$; thus the contribution of the ion at $\mathbf{R} + \mathbf{d}_j$ to the electronic charge density of the crystal is $\rho_j(\mathbf{r} - [\mathbf{R} + \mathbf{d}_j])$. (The electronic charge is usually factored out of the atomic form factor to make it dimensionless.)

[11] As a result we have been unable to make precise statements about the absolute intensity of the Bragg peaks, or about the diffuse background of radiation in directions not allowed by the Bragg condition.

[12] Considered quantum mechanically, a particle of momentum p can be viewed as a wave of wavelength $\lambda = h/p$.

Figure 6.13
Schematic view of a Debye-Scherrer camera.
Diffraction peaks are recorded on the film strip.
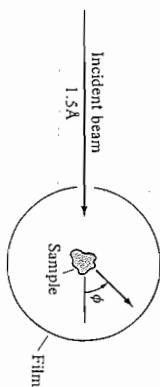
2. It is often convenient to represent a face-centered cubic Bravais lattice as simple cubic, with a cubic primitive cell of side a and a four-point basis.

(a) Show that the structure factor (6.13) is then either 4 or 0 at all points of the simple cubic reciprocal lattice.

(b) Show that when points with zero structure factor are removed, the remaining points of the reciprocal lattice make up a body-centered cubic lattice with conventional cell of side $4\pi/a$. Why is this to be expected?

3. (a) Show that the structure factor for a monatomic hexagonal close-packed crystal structure can take on any of the six values $1 + e^{i\pi n/3}$, $n = 1, \ldots, 6$, as $\mathbf{K}$ ranges through the points of the simple hexagonal reciprocal lattice.

(b) Show that all reciprocal lattice points have nonvanishing structure factor in the plane perpendicular to the c-axis containing $\mathbf{K} = 0$.

(c) Show that points of zero structure factor are found in alternate planes in the family of reciprocal lattice planes perpendicular to the c-axis.

(d) Show that in such a plane the point that is displaced from $\mathbf{K} = 0$ by a vector parallel to the c-axis has zero structure factor.

(e) Show that the removal of all points of zero structure factor from such a plane reduces the triangular network of reciprocal lattice points to a honeycomb array (Figure 4.3).

4. Consider a lattice with an n-ion basis. Suppose that the ith ion in the basis, when translated to $\mathbf{r} = 0$, can be regarded as composed of m_i point particles of charge $-z_{ij}e$, located at positions $\mathbf{b}_{ij}$, $j = 1, \ldots, m_i$.

(a) Show that the atomic form factor f_i is given by

$$f_i = \sum_{j=1}^{m_i} z_{ij} e^{i\mathbf{K}\cdot\mathbf{b}_{ij}}. \qquad (6.23)$$

(b) Show that the total structure factor (6.21) implied by (6.23) is identical to the structure factor one would have found if the lattice were equivalently described as having a basis of $m_1 + \cdots + m_n$ point ions.

5. (a) The sodium chloride structure (Figure 4.24) can be regarded as an fcc Bravais lattice of cube side a, with a basis consisting of a positively charged ion at the origin and a negatively charged ion at $(a/2)\hat{\mathbf{x}}$. The reciprocal lattice is body-centered cubic, and the general reciprocal lattice vector has the form (6.19), with all the coefficients ν_i either integers or integers $+\frac{1}{2}$. If the atomic form factors for the two ions are f_+ and f_-, show that the structure factor is $S_\mathbf{K} = f_+ + f_-$, if the ν_i are integers, and $f_+ - f_-$, if the ν_i are integers $+\frac{1}{2}$. (Why does $S_\mathbf{K}$ vanish in the latter case when $f_+ = f_-$?)

(b) The zincblende structure (Figure 4.18) is also a face-centered cubic Bravais lattice of cube side a, with a basis consisting of a positively charged ion at the origin and a negatively charged

ion at $(a/4)(\hat{x} + \hat{y} + \hat{z})$. Show that the structure factor S_K is $f_+ \pm if_-$ if the ν_i are integers $+ \frac{1}{4}$, $f_+ + f_-$ if the ν_i are integers and $\Sigma\nu_i$ is even, and $f_+ - f_-$ if the ν_i are integers and $\Sigma\nu_i$ is odd.

(c)   Suppose that a cubic crystal is known to be composed of closed-shell (and hence spherically symmetric) ions, so that $f_\pm$ (K) depends only on the magnitude of K. The positions of the Bragg peaks reveal that the Bravais lattice is face-centered cubic. Discuss how one might determine, from the structure factors associated with the Bragg peaks, whether the crystal structure was likely to be of the sodium chloride or zincblende type.

7
Classification of Bravais Lattices and Crystal Structures

Symmetry Operations and the Classification of Bravais Lattices

The Seven Crystal Systems and Fourteen Bravais Lattices

Crystallographic Point Groups and Space Groups

Schoenflies and International Notations

Examples from the Elements

In Chapters 4 and 5, only the *translational* symmetries of Bravais lattices were described and exploited. For example, the existence and basic properties of the reciprocal lattice depend only on the existence of three primitive direct lattice vectors a_i, and not on any special relations that may hold among them.[1] The translational symmetries are by far the most important for the general theory of solids. It is nevertheless clear from examples already described that Bravais lattices do fall naturally into categories on the basis of symmetries other than translational. Simple hexagonal Bravais lattices, for example, regardless of the c/a ratio, bear a closer resemblance to one another than they do to any of the three types of cubic Bravais lattice we have described.

It is the subject of crystallography to make such distinctions systematic and precise.[2] Here we shall only indicate the basis for the rather elaborate crystallographic classifications, giving some of the major categories and the language by which they are described. In most applications what matters are the features of particular cases, rather than a systematic general theory, so few solid state physicists need master the full analysis of crystallography. Indeed, the reader with little taste for the subject can skip this chapter entirely with little loss in understanding what follows, referring back to it on occasion for the elucidation of arcane terms.

THE CLASSIFICATION OF BRAVAIS LATTICES

The problem of classifying all possible crystal structures is too complex to approach directly, and we first consider only the classification of Bravais lattices.[3] From the point of view of symmetry, a Bravais lattice is characterized by the specification of all rigid operations[4] that take the lattice into itself. This set of operations is known as the *symmetry group* or *space group* of the Bravais lattice.[5]

The operations in the symmetry group of a Bravais lattice include all translations through lattice vectors. In addition, however, there will in general be rotations, reflections, and inversions[6] that take the lattice into itself. A cubic Bravais lattice, for example, is taken into itself by a rotation through 90° about a line of lattice points in a ⟨100⟩ direction, a rotation through 120° about a line of lattice points in a ⟨111⟩ direction, reflection of all points in a {100} lattice plane, etc.; a simple hexagonal Bravais lattice is taken into itself by a rotation through 60° about a line of lattice points parallel to the c-axis, reflection in a lattice plane perpendicular to the c-axis, etc.

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[1] An example of such a relation is the orthonormality condition $a_i \cdot a_j = a^2 \delta_{ij}$, holding for the appropriate primitive vectors in a simple cubic Bravais lattice.

[2] A detailed view of the subject can be found in M. J. Buerger, *Elementary Crystallography*, Wiley, New York, 1963.

[3] In this chapter a Bravais lattice is viewed as the crystal structure formed by placing at each point of an abstract Bravais lattice a basis of maximum possible symmetry (such as a sphere, centered on the lattice point) so that no symmetries of the point Bravais lattice are lost because of the insertion of the basis.

[4] Operations that preserve the distance between all lattice points.

[5] We shall avoid the language of mathematical group theory, since we shall make no use of the analytical conclusions to which it leads.

[6] Reflection in a plane replaces an object by its mirror image in that plane; inversion in a point P takes the point with coordinates r (with respect to P as origin) into $-r$. All Bravais lattices have inversion symmetry in any lattice point (Problem 1).

Any symmetry operation of a Bravais lattice can be compounded out of a translation T_R through a lattice vector R and a rigid operation leaving at least one lattice point fixed.[7] This is not immediately obvious. A simple cubic Bravais lattice, for example, is left fixed by a rotation through 90° about a ⟨100⟩ axis that passes through the center of a cubic primitive cell with lattice points at the eight vertices of the cube. This is a rigid operation that leaves no lattice points at a lattice point fixed. However, it can be compounded out of a translation through a Bravais lattice vector and a rotation

about a line of lattice points, as illustrated in Figure 7.1. That such a representation is always possible can be seen as follows:

Consider a symmetry operation S that leaves *no* lattice point fixed. Suppose it takes the origin of the lattice O into the point R. Consider next the operation one gets by first applying S, and then applying a translation through $-R$, which we denote by T_{-R}. The composite operation, which we call $T_{-R}S$, is also a symmetry of the lattice, but it leaves the origin fixed, since S transports the origin to R while T_{-R} carries R back to the origin. Thus $T_{-R}S$ is an operation that leaves at least one lattice point (namely the origin) fixed. If, however, after performing the operation $T_{-R}S$ we then perform the operation T_R, the result is equivalent to the operation S alone, since the final application of T_R just undoes the preceding application of T_{-R}. Therefore S can be compounded out of $T_{-R}S$, which leaves a point fixed, and T_R, which is a pure translation.
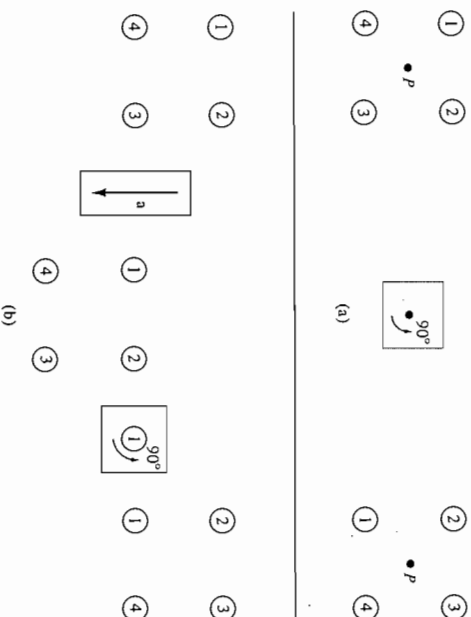
Figure 7.1
(a) A simple cubic lattice is carried into itself by a rotation through 90° about an axis that contains no lattice points. The rotation axis is perpendicular to the page, and only the four lattice points closest to the axis in a single lattice plane are shown. (b) Illustrating how the same final result can be compounded out of (at left) a translation through a lattice constant and (at right) a rotation about the lattice point numbered 1.

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[7] Note that translation through a lattice vector (other than **O**) leaves no point fixed.

Thus the full symmetry group of a Bravais lattice[8] contains only operations of the following form:

1. Translations through Bravais lattice vectors;
2. Operations that leave a particular point of the lattice fixed;
3. Operations that can be constructed by successive applications of the operations of type (1) or (2).

The Seven Crystal Systems

When examining nontranslational symmetries, one often considers not the entire space group of a Bravais lattice, but only those operations that leave a particular point fixed (i.e., the operations in category (2) above). This subset of the full symmetry group of the Bravais lattice is called the *point group* of the Bravais lattice.

There turn out to be only seven distinct point groups that a Bravais lattice can have.[9] Any crystal structure belongs to one of *seven crystal systems*, depending on which of these seven point groups is the point group of its underlying Bravais lattice. The seven crystal systems are enumerated in the next section.
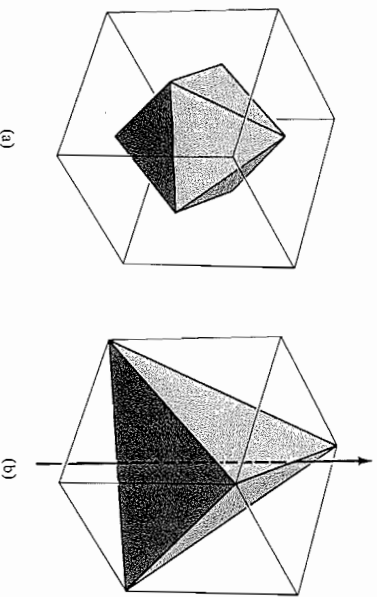
Figure 7.2
(a) Every symmetry operation of a cube is also a symmetry operation of a regular octahedron, and vice versa. Thus the cubic group is identical to the octahedral group. (b) Not every symmetry operation of a cube is a symmetry operation of a regular tetrahedron. For example, rotation through 90° about the indicated vertical axis takes the cube into itself, but not the tetrahedron.

(a)   (b)

---

[8] We shall see below that a general crystal structure can have additional symmetry operations that are not of types (1), (2), or (3). They are known as "screw axes" and "glide planes."

[9] Two point groups are identical if they contain precisely the same operations. For example, the set of all symmetry operations of a cube is identical to the set of all symmetry operations of a regular octahedron, as can readily be seen by inscribing the octahedron suitably in the cube (Figure 7.2a). On the other hand, the symmetry group of the cube is not equivalent to the symmetry group of the regular tetrahedron. The cube has more symmetry operations (Figure 7.2b).

The Fourteen Bravais Lattices

When one relaxes the restriction to point operations and considers the full symmetry group of the Bravais lattice, there turn out to be fourteen distinct space groups that a Bravais lattice can have.[10] Thus, from the point of view of symmetry, there are fourteen different kinds of Bravais lattice. This enumeration was first done by M. L. Frankheim (1842). Frankheim miscounted, however, reporting fifteen possibilities. A. Bravais (1845) was the first to count the categories correctly.

Enumeration of the Seven Crystal Systems and Fourteen Bravais Lattices

We list below the seven crystal systems and the Bravais lattices belonging to each. The number of Bravais lattices in a system is given in parentheses after the name of the system:

Cubic (3)   The cubic system contains those Bravais lattices whose point group is just the symmetry group of a cube (Figure 7.3a). Three Bravais lattices with nonequivalent space groups all have the cubic point group. They are the *simple cubic, body-centered cubic,* and *face-centered cubic.* All three have been described in Chapter 4.

Tetragonal (2)   One can reduce the symmetry of a cube by pulling on two opposite faces to stretch it into a rectangular prism with a square base, but a height not equal to the sides of the square (Figure 7.3b). The symmetry group of such an object is the tetragonal group. By so stretching the simple cubic Bravais lattice one constructs the *simple tetragonal* Bravais lattice, which can be characterized as a Bravais lattice generated by three mutually perpendicular primitive vectors, only two of which are of equal length. The third axis is called the c-axis. By similarly stretching the body-centered and face-centered cubic lattices only one more Bravais lattice of the tetragonal system is constructed, the *centered tetragonal.*

To see why there is no distinction between body-centered and face-centered tetragonal, consider Figure 7.4a, which is a representation of a centered tetragonal Bravais lattice viewed along the c-axis. The points 2 lie in a lattice plane a distance

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[10] The equivalence of two Bravais lattice space groups is a somewhat more subtle notion than the equivalence of two point groups (although both reduce to the concept of "isomorphism" in abstract group theory). It is no longer enough to say that two space groups are equivalent if they have the same operations, for the operations of identical space groups can differ in inconsequential ways. For example, two simple cubic Bravais lattices with different lattice constants, a and a', are considered to have the same space groups even though the translations in one are in steps of a, whereas the translations in the other are in steps of a'. Similarly, we would like to regard all simple hexagonal Bravais lattices as having identical space groups, regardless of the value of c/a, which is clearly irrelevant to the total symmetry of the structure.

We can get around this problem by noting that in such cases one can continuously deform a structure of a given type into another of the same type without ever losing any of the symmetry operations along the way. Thus one can uniformly expand the cube axes from a to a', always maintaining the simple cubic symmetry, or one can stretch (or shrink) the c-axis (or a-axis), always maintaining the simple hexagonal symmetry. Therefore two Bravais lattices can be said to have the same space group if it is possible continuously to transform one into the other in such a way that every symmetry operation of the first is continuously transformed into a symmetry operation of the second, and there are no additional symmetry operations of the second not so obtained from symmetry operations of the first.
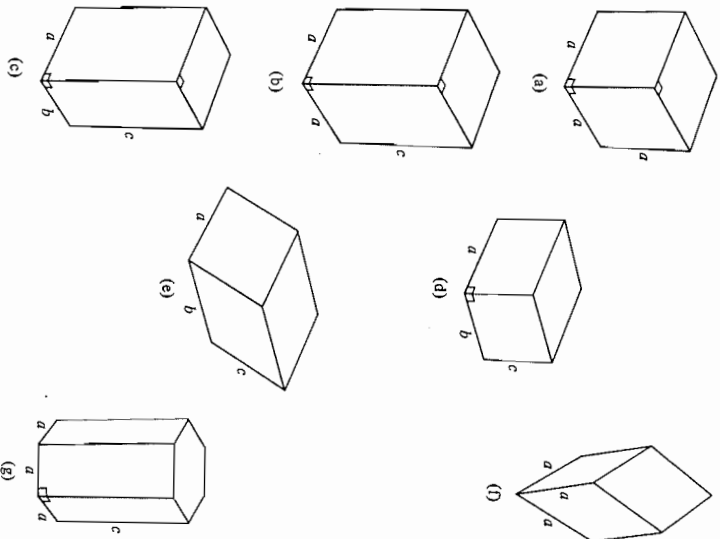
(a)

(b)

(c)

(d)

(e)

(f)

(g)

Figure 7.3
Objects whose symmetries are the point-group symmetries of Bravais lattices belonging to the seven crystal systems: (a) cubic; (b) tetragonal; (c) orthorhombic; (d) monoclinic; (e) triclinic; (f) trigonal; (g) hexagonal.

$c/2$ from the lattice plane containing the points 1. If $c = a$, the structure is nothing but a body-centered cubic Bravais lattice, and for general c it can evidently be viewed as the result of stretching the bcc lattice along the c-axis, as in Figure 7.4b, with the lattice planes regarded as centered square arrays of side $a' = \sqrt{2}a$. If $c = a'/2 = a/\sqrt{2}$, the structure is nothing but a face-centered cubic Bravais lattice, and for general c it can therefore be viewed as the result of stretching the fcc lattice along the c-axis.

Putting it the other way around, face-centered cubic and body-centered cubic are both special cases of centered tetragonal, in which the particular value of the c/a ratio introduces extra symmetries that are revealed most clearly when one views the lattice as in Figure 7.4a (bcc) or Figure 7.4b (fcc).

Orthorhombic (4) Continuing to still less symmetric deformations of the cube, one can reduce tetragonal symmetry by deforming the square faces of the object in Figure 7.3b into rectangles, producing an object with mutually perpendicular sides of three unequal lengths (Figure 7.3c). The orthorhombic group is the symmetry group of such an object. By stretching a simple tetragonal lattice along one of the a-axes (Figure 7.5a and b), one produces the *simple orthorhombic* Bravais lattice. However, by stretching the simple tetragonal lattice along a square diagonal (Figure 7.5c and d) one produces a second Bravais lattice of orthorhombic point group symmetry, the *base-centered orthorhombic*.

(a)

(b)
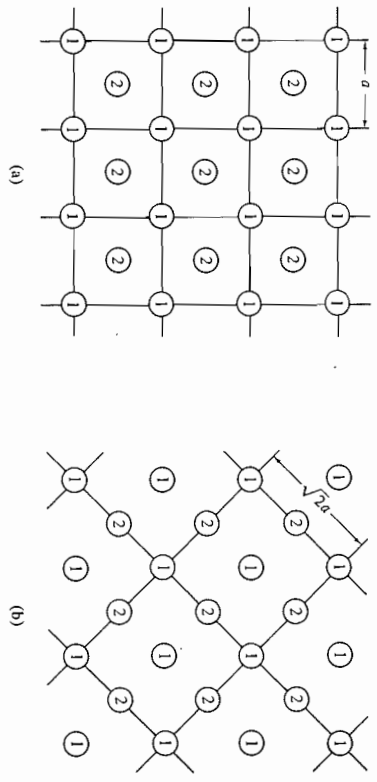
Figure 7.4
Two ways of viewing the same centered tetragonal Bravais lattice. The view is along the c-axis. The points labeled 1 lie in a lattice plane perpendicular to the c-axis, and the points labeled 2 lie in a parallel lattice plane a distance $c/2$ away. In (a) the points 1 are viewed as a simple square array, stressing that centered tetragonal is a distortion of body-centered cubic. In (b) the points 1 are viewed as a centered square array, stressing that centered tetragonal is also a distortion of face-centered cubic.

(a)

(b)

(c)

(d)
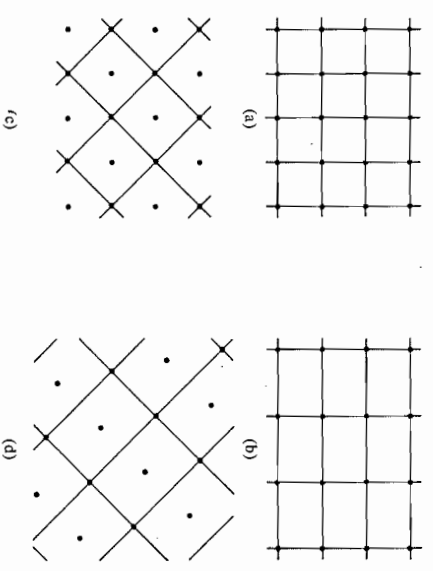
Figure 7.5
Two ways of deforming the same simple tetragonal Bravais lattice. The view is along the c-axis, and a single lattice plane is shown. In (a) bonds are drawn to emphasize that the points in the plane can be viewed as a simple square array. Stretching along a side of that array leads to the rectangular nets (b), stacked directly above one another. The resulting Bravais lattice is simple orthorhombic. In (c) lines are drawn to emphasize that the same array of points as shown in (a) can also be viewed as a centered square array. Stretching along a side of that array (i.e., along a diagonal of the square array emphasized in (a)) yields the centered rectangular nets (d), stacked directly above one another. The resulting Bravais lattice is base-centered orthorhombic.

In the same way, one can reduce the point symmetry of the centered tetragonal lattice to orthorhombic in two ways, stretching either along one set of parallel lines drawn in Figure 7.4a to produce *body-centered orthorhombic*, or along one set of parallel lines in Figure 7.4b, producing *face-centered orthorhombic*.

These four Bravais lattices exhaust the orthorhombic system.

Monoclinic (2) One can reduce orthorhombic symmetry by distorting the rectangular faces perpendicular to the c-axis in Figure 7.3c into general parallelograms. The symmetry group of the resulting object (Figure 7.3d) is the monoclinic group. By so distorting the simple orthorhombic Bravais lattice one produces the *simple monoclinic* Bravais lattice, which has no symmetries other than those required by the fact that it can be generated by three primitive vectors, one of which is perpendicular to the plane of the other two. Similarly, distorting the base-centered orthorhombic Bravais lattice produces a lattice with the same simple monoclinic space group. However, so distorting either the face-centered or body-centered orthorhombic Bravais lattices produces the *centered monoclinic* Bravais lattice (Figure 7.6).
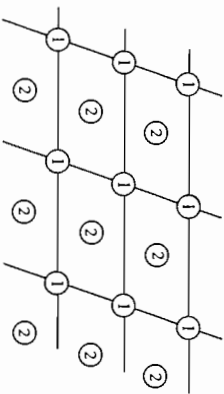
Figure 7.6
View along the c-axis of a centered monoclinic Bravais lattice. The points labeled 1 lie in a lattice plane perpendicular to the c-axis. The points labeled 2 lie in a parallel lattice plane a distance $c/2$ away, and are directly above the centers of the parallelograms formed by the points 1.

Note that the two monoclinic Bravais lattices correspond to the two tetragonal ones. The doubling in the orthorhombic case reflects the fact that a rectangular net and a centered rectangular net have distinct two-dimensional symmetry groups, while a square net and centered square net are not distinct, nor are a parallelogram net and centered parallelogram net.

Triclinic (1) The destruction of the cube is completed by tilting the c-axis in Figure 7.3d so that it is no longer perpendicular to the other two, resulting in the object pictured in Figure 7.3e, upon which there are no symmetries except that pairs of opposite faces are parallel. By so distorting either monoclinic Bravais lattice one constructs the *triclinic* Bravais lattice. This is the Bravais lattice generated by three primitive vectors with no special relationships to one another, and is therefore the Bravais lattice of minimum symmetry. The triclinic point group is not, however, the group of an object without any symmetry, since any Bravais lattice is invariant under an inversion in a lattice point. That, however, is the only symmetry required by the general definition of a Bravais lattice, and therefore the only operation[11] in the triclinic point group.

By so torturing a cube we have arrived at twelve of the fourteen Bravais lattices and five of the seven crystal systems. We can find the thirteenth and sixth by returning to the original cube and distorting it differently:

[11] Other than the identity operation (which leaves the lattice where it is), which is always counted among the members of a symmetry group.

Trigonal (1) The trigonal point group describes the symmetry of the object one produces by stretching a cube along a body diagonal (Figure 7.3f). The lattice made by so distorting any of the three cubic Bravais lattices is the *rhombohedral* (or *trigonal*) Bravais lattice. It is generated by three primitive vectors of equal length that make equal angles with one another.[12]

Finally, unrelated to the cube, is:

Hexagonal (1) The hexagonal point group is the symmetry group of a right prism with a regular hexagon as base (Figure 7.3g). The *simple hexagonal* Bravais lattice (described in Chapter 4) has the hexagonal point group and is the only Bravais lattice in the hexagonal system.[13]

The seven crystal systems and fourteen Bravais lattices described above exhaust the possibilities. This is far from obvious (or the lattices would have been known as Frankheim lattices). However, it is of no practical importance to understand why these are the only distinct cases. It is enough to know why the categories exist, and what they are.

THE CRYSTALLOGRAPHIC POINT GROUPS AND SPACE GROUPS

We next describe the results of a similar analysis, applied not to Bravais lattices but to general crystal structures. We consider the structure obtained by translating an arbitrary object through the vectors of any Bravais lattice, and try to classify the symmetry groups of the arrays so obtained. These depend both on the symmetry of the object and the symmetry of the Bravais lattice. Because the objects are no longer required to have maximum (e.g., spherical) symmetry, the number of symmetry groups is greatly increased: there turn out to be 230 different symmetry groups that a lattice with a basis can have, known as the 230 *space groups*. (This is to be compared with the fourteen space groups that result when the basis is required to be completely symmetric.)

The possible point groups of a general crystal structure have also been enumerated. These describe the symmetry operations that take the crystal structure into itself while leaving one point fixed (i.e., the nontranslational symmetries). There are thirty-two distinct point groups that a crystal structure can have, known as the *thirty-two crystallographic point groups*. (This is to be compared with the seven point groups one can have when the basis is required to have full symmetry.)

These various numbers and their relations to one another are summarized in Table 7.1.

The thirty-two crystallographic point groups can be constructed out of the seven Bravais lattice point groups by systematically considering all possible ways of reducing the symmetry of the objects (Figure 7.3) characterized by these groups. Each of the twenty-five new groups constructed in this way is associated with one

[12] Special values of that angle may introduce extra symmetries, in which case the lattice may actually be one of the three cubic types. See, for example, Problem 2(a).

[13] If one tries to produce further Bravais lattices from distortions of the simple hexagonal, one finds that changing the angle between the two primitive vectors of equal length perpendicular to the c-axis yields a base-centered orthorhombic lattice, changing their magnitudes as well leads to monoclinic, and tilting the c-axis from the perpendicular leads, in general, to triclinic.

Table 7.1
POINT AND SPACE GROUPS OF BRAVAIS LATTICES AND CRYSTAL STRUCTURES

	BRAVAIS LATTICE (BASIS OF SPHERICAL SYMMETRY)	CRYSTAL STRUCTURE (BASIS OF ARBITRARY SYMMETRY)
Number of point groups:	7 ("the 7 crystal systems")	32 ("the 32 crystallographic point groups")
Number of space groups:	14 ("the 14 Bravais lattices")	230 ("the 230 space groups")

Figure 7.7
The hierarchy of symmetries among the seven crystal systems. Each Bravais lattice point group contains all those that can be reached from it by moving in the direction of the arrows.

of the seven crystal systems according to the following rule: Any group constructed by reducing the symmetry of an object characterized by a particular crystal system continues to belong to that system until the symmetry has been reduced so far that all of the remaining symmetry operations of the object are also found in a less symmetrical crystal system; when this happens the symmetry group of the object is assigned to the less symmetrical system. Thus the crystal system of a crystallographic point group is that of the least symmetrical[14] of the seven Bravais lattice point groups containing every symmetry operation of the crystallographic group.
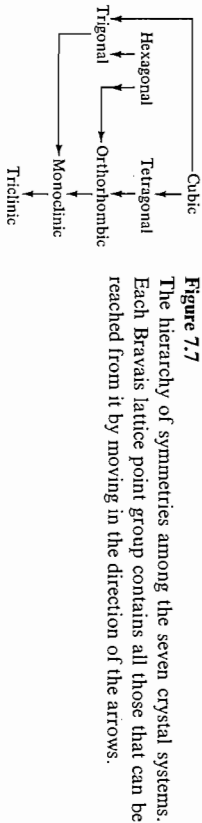
Objects with the symmetries of the five crystallographic point groups in the cubic system are pictured in Table 7.2. Objects with the symmetries of the twenty-seven noncubic crystallographic groups are shown in Table 7.3.

Crystallographic point groups may contain the following kinds of symmetry operations:

1. **Rotations through Integral Multiples of $2\pi/n$ about Some Axis** The axis is called an n-fold rotation axis. It is easily shown (Problem 6) that a Bravais lattice can

14 The notion of a hierarchy of crystal system symmetries needs some elaboration. In Figure 7.7 each crystal system is more symmetric than any that can be reached from it by moving along arrows; i.e., the corresponding Bravais lattice point group has no operations that are not also in the groups from which it can be so reached. There appears to be some ambiguity in this scheme since the four pairs cubic-hexagonal, tetragonal-hexagonal, tetragonal-trigonal, and orthorhombic-trigonal are not ordered by the arrows. Thus one might imagine an object all of whose symmetry operations belonged to both the tetragonal and trigonal groups but to no group lower than both of these. The symmetry group of such an object could be said to belong to either the tetragonal or trigonal systems, since there would be no unique system of lowest symmetry. It turns out, however, both in this and the other three ambiguous cases, that all symmetry elements common to both groups in a pair also belong to a group that is lower than both in the hierarchy. (For example, any element common to both the tetragonal and the trigonal groups also belongs to the monoclinic group.) There is therefore always a unique group of lowest symmetry.

Table 7.2
OBJECTS WITH THE SYMMETRY OF THE FIVE CUBIC CRYSTALLOGRAPHIC POINT GROUPS[a]
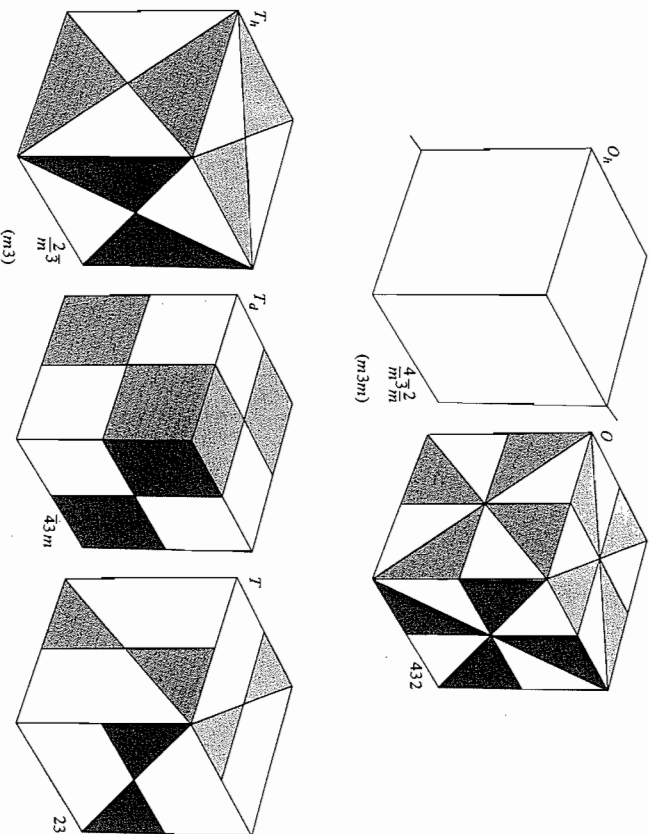
a To the left of each object is the Schoenflies name of its symmetry group and to the right is the international name. The unpictured faces may be deduced from the fact that rotation about a body diagonal through 120° is a symmetry operation for all five objects. (Such an axis is shown on the undecorated cube.)

contain only 2-, 3-, 4-, or 6-fold axes. Since the crystallographic point groups are contained in the Bravais lattice point groups, they too can only have these axes.

2. **Rotation-Reflections** Even when a rotation through $2\pi/n$ is not a symmetry element, sometimes such a rotation followed by a reflection in a plane perpendicular to the axis may be. The axis is then called an n-fold rotation-reflection axis. For example, the groups S_6 and S_4 (Table 7.3) have 6- and 4-fold rotation-reflection axes.

3. **Rotation-Inversions** Similarly, sometimes a rotation through $2\pi/n$ followed by an inversion in a point lying on the rotation axis is a symmetry element, even though such a rotation by itself is not. The axis is then called an n-fold rotation-inversion axis. The axis in S_4 (Table 7.3), for example, is also a 4-fold rotation-inversion axis. However, the axis in S_6 is only a 3-fold rotation-inversion axis.

4. **Reflections** A reflection takes every point into its mirror image in a plane, known as a mirror plane.

Table 7.3
THE NONCUBIC CRYSTALLOGRAPHIC POINT GROUPS [a]

SCHOEN-FLIES	HEXAGONAL	TETRAGONAL	TRIGONAL	ORTHO-RHOMBIC	MONOCLINIC	TRICLINIC	INTER-NATIONAL
C_n	C_6 6	C_4 4	C_3 3		C_2 2	C_1 1	n
C_{nv}	C_{6v} 6mm	C_{4v} 4mm	C_{3v} 3m	C_{2v} 2mm			nmm (n even) nm (n odd)
C_{nh}	C_{6h} 6/m	C_{4h} 4/m	C_{3h} $\bar{6}$		C_{2h} 2/m C_{1h} m ($\bar{2}$)		n/m
S_n		S_4 $\bar{4}$	S_6 $\bar{3}$ (C_{3i})			S_2 (C_i) $\bar{1}$	$\bar{n}$
D_n	D_6 622	D_4 422	D_3 32	D_2 (V) 222			n2 (n odd) n22 (n even)
D_{nh}	D_{6h} 6/mmm D_{3h} $\bar{6}2m$	D_{4h} 4/mmm		D_{2h} (V_h) 2/mmm mmm			$\frac{n}{m}\frac{2}{m}\frac{2}{m}$ (n even) $\bar{n}2m$ (n odd)
D_{nd}		D_{2d} (V_d) $\bar{4}2m$	D_{3d} $\bar{3}\frac{2}{m}$ ($\bar{3}m$)				$\bar{n}2m$ (n even) $\bar{n}\frac{2}{m}$ (n odd)

[a] Table caption on p. 123.

Table 7.3 (*continued*)

The unpictured faces can be deduced by imagining the representative objects to be rotated about the n-fold axis, which is always vertical. The Schoenflies name of the group is given to the left of the representative object, and the international designation the right. The groups are organized into vertical columns by crystal system, and into horizontal rows by the Schoenflies or international type. Note that the Schoenflies categories (given on the extreme left of the table) divide up the groups somewhat differently from the international categories (given on the extreme right). In most (but not all) cases the representative objects have been made by simply decorating the appropriate symmetry reducing manner the faces of the objects used to represent the crystal systems (Bravais lattice point groups) in Figure 7.3. Exceptions are the trigonal groups and two of the hexagonal groups, where the figures have been changed to emphasize the similarity within the (horizontal) Schoenflies categories. For a representation of the trigonal groups by decorations of the object in Figure 7.3f, see Problem 4.

5. **Inversions**   An inversion has a single fixed point. If that point is taken into the origin, then every other point **r** is taken into **−r**.

Point-Group Nomenclature

Two nomenclatural systems, the Schönflies and the international, are in wide use. Both designations are given in Tables 7.2 and 7.3.

Schoenflies Notation for the Noncubic Crystallographic Point Groups   The Schoenflies categories are illustrated by grouping the rows in Table 7.3 according to the labels given on the left side. They are:[15]

C_n: These groups contain only an n-fold rotation axis.

C_{nv}: In addition to the n-fold axis, these groups have a mirror plane that contains the axis of rotation, plus as many additional mirror planes as the n-fold axis requires.

C_{nh}: These groups contain in addition to the n-fold axis, a single mirror plane that is perpendicular to the axis.

S_n: These groups contain only an n-fold rotation-reflection axis.

D_n: In addition to an n-fold rotation axis, these groups contain a 2-fold axis perpendicular to the n-fold axis, plus as many additional 2-fold axes as are required by the existence of the n-fold axis.

D_{nh}: These (the most symmetric of the groups) contain all the elements of D_n plus a mirror plane perpendicular to the n-fold axis.

D_{nd}: These contain the elements of D_n plus mirror planes containing the n-fold axis, which bisect the angles between the 2-fold axes.

It is instructive to verify that the objects shown in Table 7.3 do indeed have the symmetries required by their Schoenflies names.

International Notation for the Noncubic Crystallographic Point Groups   The international categories are illustrated by grouping the rows in Table 7.3 according to

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[15] C stands for "cyclic," D for "dihedral," and S for "Spiegel" (mirror). The subscripts h, v, and d stand for "horizontal," "vertical," and "diagonal," and refer to the placement of the mirror planes with respect to the n-fold axis, considered to be vertical. (The "diagonal" planes in D_{nd} are vertical and bisect the angles between the 2-fold axes.)

the labels given on the right side. Three categories are identical to the Schoenflies categories:

n is the same as C_n.

nmm is the same as C_{nv}. The two m's refer to two distinct types of mirror planes containing the n-fold axis. What they are is evident from the objects illustrating $6mm$, $4mm$, and $2mm$. These demonstrate that a $2j$-fold axis takes a vertical mirror plane into j mirror planes, but in addition j others automatically appear, bisecting the angles between adjacent planes in the first set. However, a $(2j + 1)$-fold axis takes a mirror plane into $2j + 1$ equivalent ones, and therefore[16] C_{3v} is only called $3m$. The discussion is the same as for nmm, but now perpendicular 2-fold axes are involved instead of vertical mirror planes.

The other international categories and their relation to those of Schoenflies are as follows:

n/m is the same as C_{nh}, except that the international system prefers to regard C_{3h} as containing a 6-fold rotation-inversion axis, making it $\bar{6}$ (see the next category). Note also that C_{1h} becomes simply m, rather than $1/m$.

$\bar{n}$ is a group with an n-fold rotation-inversion axis. This category contains C_{3h}, disguised as $\bar{6}$. It also contains S_4, which goes nicely into $\bar{4}$. However, S_6 becomes $\bar{3}$ and S_2 becomes $\bar{1}$ by virtue of the difference between rotation-reflection and rotation-inversion axes.

$\frac{n}{m} \frac{2}{m} \frac{2}{m}$, abbreviated n/mmm, is just D_{nh}, except that the international system prefers to regard D_{3h} as containing a 6-fold rotation-inversion axis, making it $\bar{6}2m$ (see the next category), and note the similarity to the ejection of C_{3h} from n/m into $\bar{n}$). Note also that $2/mmm$ is conventionally abbreviated further into mmm. The full-blown international title is supposed to remind one that D_{nh} can be viewed as an n-fold axis with a perpendicular mirror plane, festooned with two sets of perpendicular 2-fold axes, each with its own perpendicular mirror planes.

$\bar{n}2m$ is the same as D_{nd}, except that D_{3h} is included as $\bar{6}2m$. The name is intended to suggest an n-fold rotation-inversion axis with a perpendicular 2-fold axis and a vertical mirror plane. The $n = 3$ case is again exceptional, the full name being $3\frac{2}{m}$ (abbreviated $\bar{3}m$) to emphasize the fact that in this case the vertical mirror plane is perpendicular to the 2-fold axis.

Nomenclature for the Cubic Crystallographic Point Groups   The Schoenflies and international names for the five cubic groups are given in Table 7.2. O_h is the full symmetry group of the cube (or octahedron, whence the O) including improper operations,[17] which the horizontal reflection plane (h) admits. O is the cubic (or octahedral) group without improper operations. T_d is the full symmetry group of the regular tetrahedron including all improper operations, T is the group of the regular tetrahedron excluding all improper operations, and T_h is what results when an inversion is added to T.

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[16] In emphasizing the differences between odd- and even-fold axes, the international system, unlike the Schoenflies, treats the 3-fold axis as a special case.

[17] Any operation that takes a right-handed object into a left-handed one is called *improper*. All others are proper. Operations containing an odd number of inversions or mirrorings are improper.

The international names for the cubic groups are conveniently distinguished from those of the other crystallographic point groups by containing 3 as a second number, referring to the 3-fold axis present in all the cubic groups.

The 230 Space Groups

We shall have mercifully little to say about the 230 space groups, except to point out that the number is larger than one might have guessed. For each crystal system one can construct a crystal structure with a different space group by placing an object with the symmetries of each of the point groups of the system into each of the Bravais lattices of the system. In this way, however, we find only 61 space groups, as shown in Table 7.4.

Table 7.4
ENUMERATION OF SOME SIMPLE SPACE GROUPS

SYSTEM	NUMBER OF POINT GROUPS	NUMBER OF BRAVAIS LATTICES	PRODUCT
Cubic	5	3	15
Tetragonal	7	2	14
Orthorhombic	3	4	12
Monoclinic	3	2	6
Triclinic	2	1	2
Hexagonal	7	1	7
Trigonal	5	1	5
Totals	32	14	61

We can eke out five more by noting that an object with trigonal symmetry yields a space group not yet enumerated, when placed in a hexagonal Bravais lattice.[18]

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[18] Although the trigonal point group is contained in the hexagonal point group, the trigonal Bravais lattice cannot be obtained from the simple hexagonal by an infinitesimal distortion. (This is in contrast to all other pairs of systems connected by arrows in the symmetry hierarchy of Figure 7.7.) The trigonal point group is contained in the hexagonal point group because the trigonal Bravais lattice can be viewed as simple hexagonal with a three-point basis consisting of

$$0; \quad \tfrac{1}{3}\mathbf{a}_1, \tfrac{1}{3}\mathbf{a}_2, \tfrac{1}{3}\mathbf{c}; \quad \text{and} \quad \tfrac{2}{3}\mathbf{a}_1, \tfrac{2}{3}\mathbf{a}_2, \tfrac{2}{3}\mathbf{c}.$$

As a result, placing a basis with a trigonal point group into a hexagonal Bravais lattice results in a different space group from that obtained by placing the same basis into a trigonal lattice. In no other case is this so. For example, a basis with tetragonal symmetry, when placed in a simple cubic lattice, yields exactly the same space group as it would if placed in a simple tetragonal lattice (unless there happens to be a special relation between the dimensions of the object and the length of the c-axis). This is reflected physically in the fact that there are crystals that have trigonal bases in hexagonal Bravais lattices, but none with tetragonal bases in cubic Bravais lattices. In the latter case there would be nothing in the structure of such an object to require the c-axis to have the same length as the a-axes; if the lattice did remain cubic it would be a mere coincidence. In contrast, a simple hexagonal Bravais lattice cannot distort continuously into a trigonal one, and can therefore be held in its simple hexagonal form even by a basis with only trigonal symmetry.

Because trigonal point groups can characterize a crystal structure with a hexagonal Bravais lattice, crystallographers sometimes maintain that there are only six crystal systems. This is because crystallography emphasizes the point symmetry rather than the translational symmetry. From the point of view of the Bravais lattice point groups, however, there are unquestionably seven crystal systems: the point groups D_{3d} and D_{6h} are both the point groups of Bravais lattices, and are not equivalent.

Table 7.7
ELEMENTS WITH ORTHORHOMBIC BRAVAIS LATTICES[a]

ELEMENT	a (Å)	b (Å)	c (Å)
Ga	4.511	4.517	7.645
P (black)	3.31	4.38	10.50
Cl (113 K)	6.24	8.26	4.48
Br (123 K)	6.67	8.72	4.48
I	7.27	9.79	4.79
S (rhombic)	10.47	12.87	24.49

[a] The lengths of the three mutually perpendicular primitive vectors are a, b, and c. The structure of rhombic sulfur is complex, with 128 atoms per unit cell. The others can be described in terms of an eight-atom unit cell. For details the reader is referred to Wyckoff.

PROBLEMS

1. (a) Prove that any Bravais lattice has inversion symmetry in a lattice point. (*Hint*: Express the lattice translations as linear combinations of primitive vectors with integral coefficients.)

(b) Prove that the diamond structure is invariant under an inversion in the midpoint of any nearest neighbor bond.

(c) Show that the diamond structure is not invariant under inversions in any other points.

2. (a) If three primitive vectors for a trigonal Bravais lattice are at angles of 90° to one another, the lattice obviously has more than trigonal symmetry, being simple cubic. Show that if the angles are 60° or arc cos $(-\frac{1}{3})$ the lattice again has more than trigonal symmetry, being face-centered cubic or body-centered cubic.

(b) Show that the simple cubic lattice can be represented as a trigonal lattice with primitive vectors $\mathbf{a}_i$ at 60° angles to one another, with a two-point basis $\pm \frac{1}{4}(\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3)$. (Compare these numbers with the crystal structures in Table 7.5.)

(c) What structure results if the basis in the same trigonal lattice is taken to be $\pm \frac{1}{8}(\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3)$?

3. If two systems are connected by arrows in the symmetry hierarchy of Figure 7.7, then a Bravais lattice in the more symmetric system can be reduced to one of lower symmetry by an infinitesimal distortion, except for the pair hexagonal-trigonal. The appropriate distortions have been fully described in the text in all cases except hexagonal-orthorhombic and trigonal-monoclinic.

(a) Describe an infinitesimal distortion that reduces a simple hexagonal Bravais lattice to one in the orthorhombic system.

(b) What kind of orthorhombic Bravais lattice can be reached in this way?

(c) Describe an infinitesimal distortion that reduces a trigonal Bravais lattice to one in the monoclinic system.

(d) What kind of monoclinic Bravais lattice can be reached in this way?

4. (a) Which of the trigonal point groups described in Table 7.3 is the point group of the Bravais lattice? That is, which of the representative objects has the symmetry of the object shown in Figure 7.3f?

(b) In Figure 7.3f the faces of the object of Figure 7.3f are decorated in various symmetry-reducing ways to produce objects with the symmetries of the remaining four trigonal point groups. Referring to Table 7.3, indicate the point-group symmetry of each object.
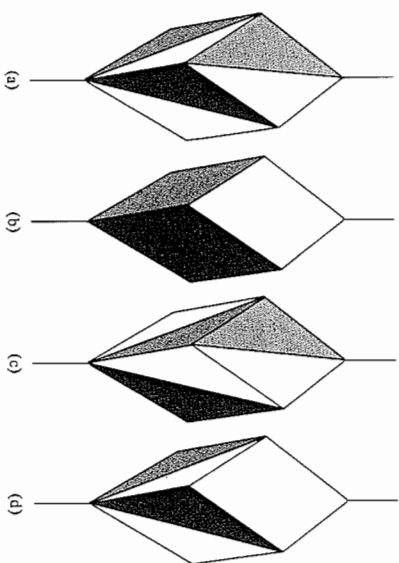
5. Which of the 14 Bravais lattices other than face-centered cubic and body-centered cubic do not have reciprocal lattices of the same kind?

6. (a) Show that there is a family of lattice planes perpendicular to any n-fold rotation axis of a Bravais lattice, $n \geq 3$. (The result is also true when $n = 2$, but requires a somewhat more elaborate argument (Problem 7).)

(b) Deduce from (a) that an n-fold axis cannot exist in any three-dimensional Bravais lattice unless it can exist in some two-dimensional Bravais lattice.

(c) Prove that no two-dimensional Bravais lattice can have an n-fold axis with $n = 5$ or $n \geq 7$. (*Hint*: First show that the axis can be chosen to pass through a lattice point. Then argue by *reductio ad absurdum*, using the set of points into which the nearest neighbor of the fixed point is taken by the n rotations to construct a point closer to the fixed point than its "nearest neighbor." (Note that the case $n = 5$ requires slightly different treatment from the others).)

7. (a) Show that if a Bravais lattice has a mirror plane, then there is a family of lattice planes parallel to the mirror plane. (*Hint*: Show from the argument on page 113 that the existence of a mirror plane implies the existence of a mirror plane containing a lattice point. It is then enough to prove that that plane contains two other lattice points not collinear with the first.)

(b) Show that if a Bravais lattice has a 2-fold rotation axis then there is a family of lattice planes perpendicular to the axis.

Figure 7.9
Objects with the symmetries of the trigonal groups of lower symmetry. Which is which?

(a)   (b)   (c)   (d)