

Crystal Structure

Having introduced a number of important ideas in one dimension, we must now deal with the fact that our world is actually spatially three-dimensional. While this adds a bit of complication, really the important concepts are no harder in three dimensions than they were in one dimension. Some of the most important ideas we have already met in one dimension, but we will reintroduce them more generally here.

There are two things that might be difficult here. First, we do need to wrestle with a bit of geometry. Hopefully most will not find this too hard. Secondly we will also need to establish a language in order to describe structures in two and three dimensions intelligently. As such, much of this chapter is just a list of definitions to be learned, but unfortunately this is necessary in order to be able to continue further at this point.

12.1 Lattices and Unit Cells

Definition 12.1 A *lattice*¹ is an infinite set of points defined by integer sums of a set of linearly independent primitive lattice² vectors.

For example, in two dimensions, as shown in Fig. 12.1 the lattice points are described as

$$\mathbf{R}_{[n_1 \ n_2]} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 \quad n_1, n_2 \in \mathbb{Z} \quad (2d)$$

with \mathbf{a}_1 and \mathbf{a}_2 being the primitive lattice vectors and n_1 and n_2 being integers. In three dimensions points of a lattice are analogously indexed by three integers:

$$\mathbf{R}_{[n_1 \ n_2 \ n_3]} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3 \quad n_1, n_2, n_3 \in \mathbb{Z} \quad (3d). \quad (12.1)$$

Note that in one dimension this definition of a lattice fits with our previous description of a lattice as being the points $R = na$ with n an integer.

It is important to point out that in two and three dimensions, the choice of primitive lattice vectors is not unique,³ as shown in Fig. 12.2. (In one dimension, the single primitive lattice vector is unique up to the sign, or direction, of a .)

³Given a set of primitive lattice vectors \mathbf{a}_i a new set of primitive lattice vectors may be constructed as $\mathbf{b}_i = \sum_j m_{ij} \mathbf{a}_j$ so long as m_{ij} is an invertible matrix with integer entries and the inverse matrix $[m^{-1}]_{ij}$ also has integer entries.

¹Warning: Some books (Ashcroft and Mermin in particular) refer to this as a *Bravais lattice*. This enables them to use the term *lattice* to describe other things that we would not call a lattice (e.g., the honeycomb). However, the definition we use here is more common among crystallographers, and more correct mathematically as well.

²Very frequently “primitive lattice vectors” are called “primitive basis vectors” (not the same use of the word “basis” as in Section 10.1) or “primitive translation vectors”.

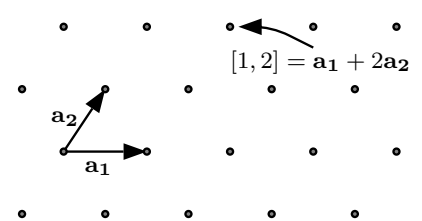


Fig. 12.1 A lattice is defined as integer sums of primitive lattice vectors.

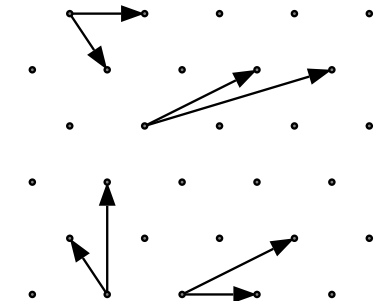


Fig. 12.2 The choice of primitive lattice vectors for a lattice is not unique. (Four possible sets of primitive lattice vectors are shown, but there are an infinite number of possibilities!)

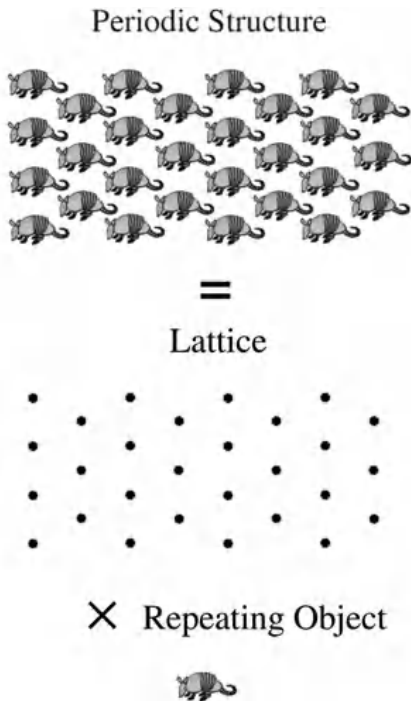


Fig. 12.3 Any periodic structure can be represented as a lattice of repeating motifs.

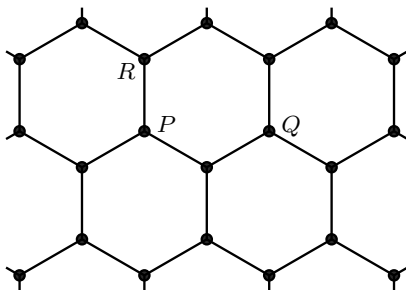


Fig. 12.4 The honeycomb is not a lattice. Points P and R are inequivalent (points P and Q are equivalent).

⁴One should be very careful *not* to call the honeycomb a hexagonal lattice. First of all, by our definition it is not a lattice at all since all points do not have the same environment. Secondly, some people (perhaps confusingly) use the term “hexagonal” to mean what the rest of us call a triangular lattice: a lattice of triangles where each point has six nearest neighbor points (see Fig. 12.6).

It turns out that there are several definitions that are entirely equivalent to the one we have just given:

Equivalent Definition 12.1.1 A *lattice* is an infinite set of vectors where addition of any two vectors in the set gives a third vector in the set.

It is easy to see that our first definition 12.1 implies the second one 12.1.1. Here is a less crisply defined, but sometimes more useful definition.

Equivalent Definition 12.1.2 A *lattice* is a set of points where the environment of any given point is equivalent to the environment of any other given point.

It turns out that any periodic structure can be expressed as a lattice of repeating motifs. A cartoon of this statement is shown in Fig. 12.3. One should be cautious however, that not all periodic arrangements of points are lattices. The honeycomb⁴ shown in Fig. 12.4 is *not* a lattice. This is obvious from the third definition 12.1.2: The environment of point P and point R are actually different—point P has a neighbor directly above it (the point R), whereas point R has no neighbor directly above.

In order to describe a honeycomb (or other more complicated arrangements of points) we have the idea of a unit cell, which we have met before in Section 10.1. Generally we have

Definition 12.2 A *unit cell* is a region of space such that when many identical units are stacked together it tiles (completely fills) all of space and reconstructs the full structure.

An equivalent (but less rigorous) definition is

Equivalent Definition 12.2.1 A *unit cell* is the repeated motif which is the elementary building block of the periodic structure.

To be more specific we frequently want to work with the smallest possible unit cell:

Definition 12.3 A *primitive unit cell* for a periodic crystal is a unit cell containing exactly one lattice point.

As mentioned in Section 10.1 the definition of the unit cell is never unique. This is shown, for example, in Fig. 12.5.

Sometimes it is useful to define a unit cell which is not primitive in order to make it simpler to work with. This is known as a *conventional unit cell*. Almost always these conventional unit cells are chosen so as to have orthogonal axes.

Some examples of possible unit cells are shown for the triangular lattice in Fig. 12.6. In this figure the conventional unit cell (upper left) is chosen to have orthogonal axes—which is often easier to work with than axes which are non-orthogonal.

A note about counting the number of lattice points in the unit cell. It is frequently the case that we will work with unit cells where the lattice

points live at the corners (or edges) of the cells. When a lattice point is on the boundary of the unit cell, it should only be counted fractionally depending on what fraction of the point is actually in the cell. So for example in the conventional unit cell shown in Fig. 12.6, there are two lattice points within this cell. There is one point in the center, then four points at the corners—each of which is one quarter inside the cell, so we obtain $2 = 1 + 4(\frac{1}{4})$ points in the cell. (Since there are two lattice points in this cell, it is by definition not primitive.) Similarly for the primitive cell shown in Fig. 12.6 (upper right), the two lattice points at the far left and the far right have a 60° degree slice (which is $\frac{1}{6}$ of a circle) inside the cell. The other two lattice points each have $\frac{1}{3}$ of the lattice point inside the unit cell. Thus this unit cell contains $2(\frac{1}{3}) + 2(\frac{1}{6}) = 1$ point, and is thus primitive. Note however, that we can just imagine shifting the unit cell a tiny amount in almost any direction such that a single lattice point is completely inside the unit cell and the others are completely outside the unit cell. This sometimes makes counting much easier.

Also shown in Fig. 12.6 is a so-called *Wigner–Seitz unit cell*

Definition 12.4 Given a lattice point, the set of all points in space which are closer to that given lattice point than to any other lattice point constitute the **Wigner–Seitz cell** of the given lattice point.⁵

There is a rather simple scheme for constructing such a Wigner–Seitz cell: choose a lattice point and draw lines to all of its possible near neighbors (not just its nearest neighbors). Then draw perpendicular bisectors of all of these lines. The perpendicular bisectors bound the Wigner–Seitz cell. It is always true that the Wigner–Seitz construction for a lattice gives a primitive unit cell. In Fig. 12.7 we show another example of the Wigner–Seitz construction for a two-dimensional lattice.

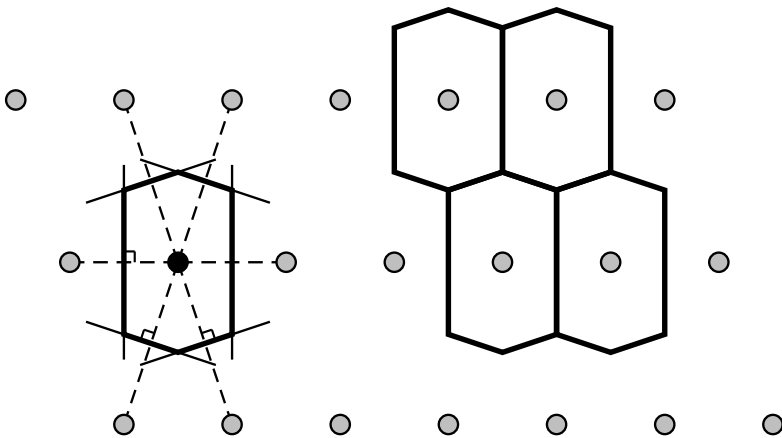


Fig. 12.7 The Wigner–Seitz construction for a lattice in two dimensions. On the left perpendicular bisectors are added between the darker point and each of its neighbors. The area bounded defines the Wigner–Seitz cell. On the right it is shown that the Wigner–Seitz cell is a primitive unit cell. (The cells on the right are exactly the same shape as the bounded area on the left!)

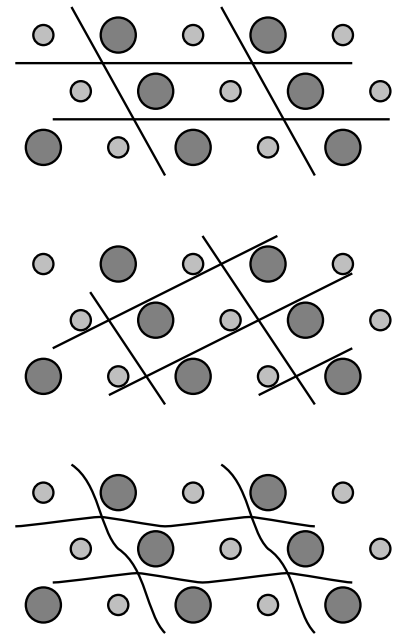


Fig. 12.5 The choice of a unit cell is not unique. All of these unit cells can be used as “tiles” to perfectly reconstruct the full crystal.

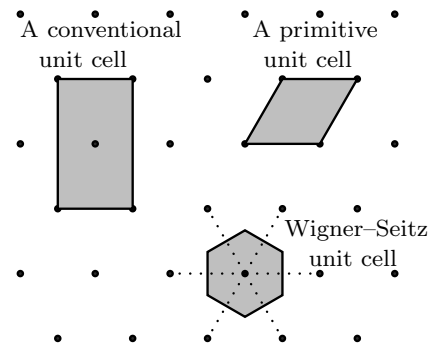


Fig. 12.6 Some unit cells for the triangular lattice.

⁵A construction analogous to Wigner–Seitz can be performed on an irregular collection of points as well as on a periodic lattice. For such an irregular set of point the region closer to one particular point than to any other of the points is known as a Voronoi cell.

⁶Eugene Wigner was yet another Nobel laureate who was one of the truly great minds of the last century of physics. Perhaps as important to physics was the fact that his sister, Margit, married Dirac. It was often said that Dirac could be a physicist only because Margit handled everything else. Fredrick Seitz was far less famous, but gained notoriety in his later years by being a consultant for the tobacco industry, a strong proponent of the Regan-era Star Wars missile defense system, and a prominent sceptic of global warming. He passed away in 2007.

A similar construction can be performed in three dimensions in which case one must construct perpendicular-bisecting planes to bound the Wigner–Seitz cell.⁶ See for example, Figs. 12.13 and 12.16.

Definition 12.5 *The description of objects in the unit cell with respect to the reference lattice point in the unit cell is known as a **basis**.*

This is the same definition of “basis” that we used in Section 10.1. In other words, we think of reconstructing the entire crystal by associating with each lattice point a basis of atoms.

In Fig. 12.8 (top) we show a periodic structure in two dimension made of two types of atoms. On the bottom we show a primitive unit cell (expanded) with the position of the atoms given with respect to the reference point of the unit cell which is taken to be the lower left-hand corner. We can describe the basis of this crystal as follows:

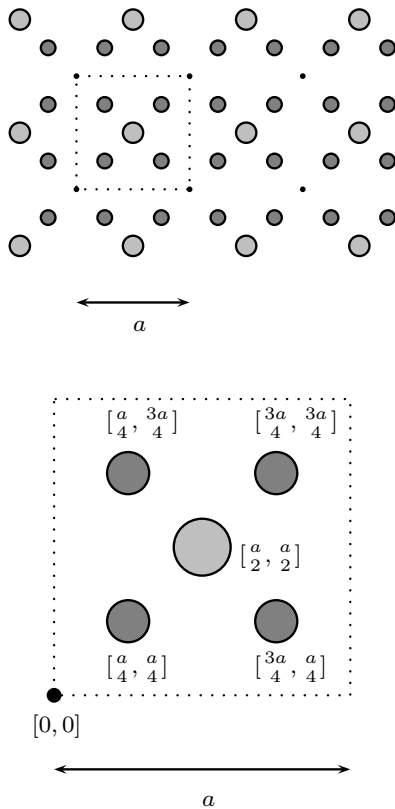


Fig. 12.8 Top: A periodic structure in two dimensions. A unit cell is marked with the dotted lines. **Bottom:** A blow-up of the unit cell with the coordinates of the objects in the unit cell with respect to the reference point in the lower left-hand corner. The basis is the description of the atoms along with these positions.

Basis for crystal in Fig. 12.8 =		
Large Light Gray Atom	Position=	$[a/2, a/2]$
Small Dark Gray Atoms	Position=	$[a/4, a/4]$
		$[a/4, 3a/4]$
		$[3a/4, a/4]$
		$[3a/4, 3a/4]$

The reference points (the small black dots in the figure) forming the square lattice have positions

$$\mathbf{R}_{[n_1 n_2]} = [a n_1, a n_2] = a n_1 \hat{x} + a n_2 \hat{y} \quad (12.2)$$

with n_1, n_2 integers so that the large light gray atoms have positions

$$\mathbf{R}_{[n_1 n_2]}^{light-gray} = [a n_1, a n_2] + [a/2, a/2]$$

whereas the small dark gray atoms have positions

$$\begin{aligned} \mathbf{R}_{[n_1 n_2]}^{dark-gray1} &= [a n_1, a n_2] + [a/4, a/4] \\ \mathbf{R}_{[n_1 n_2]}^{dark-gray2} &= [a n_1, a n_2] + [a/4, 3a/4] \\ \mathbf{R}_{[n_1 n_2]}^{dark-gray3} &= [a n_1, a n_2] + [3a/4, a/4] \\ \mathbf{R}_{[n_1 n_2]}^{dark-gray4} &= [a n_1, a n_2] + [3a/4, 3a/4]. \end{aligned}$$

In this way you can say that the positions of the atoms in the crystal are “the lattice plus the basis”.

We can now return to the case of the honeycomb shown in Fig. 12.4. The same honeycomb is shown in Fig. 12.9 with the lattice and the basis explicitly shown. Here, the reference points (small black dots) form a

(triangular) lattice, where we can write the primitive lattice vectors as

$$\begin{aligned} \mathbf{a}_1 &= a \hat{x} \\ \mathbf{a}_2 &= (a/2) \hat{x} + (a\sqrt{3}/2) \hat{y}. \end{aligned} \tag{12.3}$$

In terms of the reference points of the lattice, the basis for the primitive unit cell, i.e., the coordinates of the two larger circles with respect to the reference point, are given by $\frac{1}{3}(\mathbf{a}_1 + \mathbf{a}_2)$ and $\frac{2}{3}(\mathbf{a}_1 + \mathbf{a}_2)$.

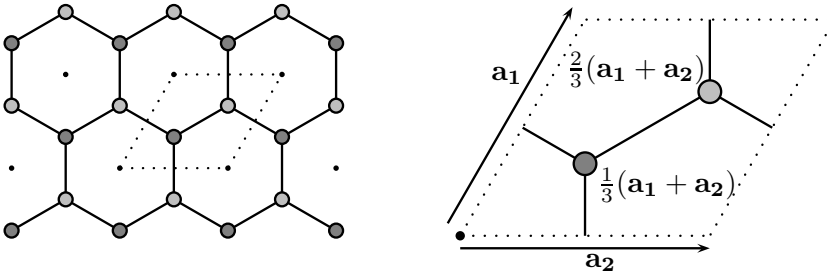


Fig. 12.9 Left: The honeycomb from Fig. 12.4 is shown with the two inequivalent points of the unit cell given different shades. The unit cell is outlined dotted and the corners of the unit cell are marked with small black dots (which form a triangular lattice). **Right:** The unit cell is expanded and coordinates are given with respect to the reference point at the lower left corner.

12.2 Lattices in Three Dimensions

The simplest lattice in three dimensions is the simple cubic lattice shown in Fig. 12.10 (sometimes known as cubic “P” or cubic-primitive lattice). The primitive unit cell in this case can most conveniently be taken to be a single cube—which includes 1/8 of each of its eight corners (see Fig. 12.11).

Only slightly more complicated than the simple cubic lattice are the *tetragonal* and *orthorhombic* lattices where the axes remain perpendicular, but the primitive lattice vectors may be of different lengths (shown in Fig. 12.11). The orthorhombic unit cell has three different lengths of its perpendicular primitive lattice vectors, whereas the tetragonal unit cell has two lengths the same and one different.

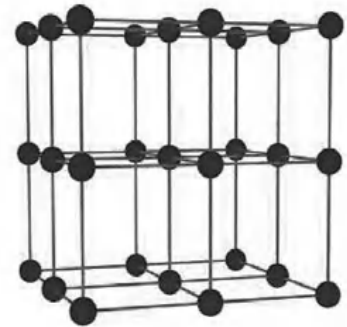


Fig. 12.10 A cubic lattice, otherwise known as cubic “P” or cubic primitive.

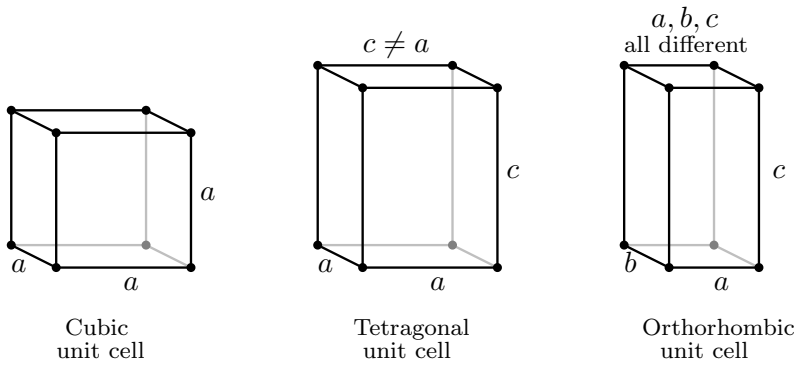


Fig. 12.11 Unit cells for cubic, tetragonal, and orthorhombic lattices.

Conventionally, to represent a given vector amongst the infinite number of possible lattice vectors in a lattice, one writes

$$[uvw] = u\mathbf{a}_1 + v\mathbf{a}_2 + w\mathbf{a}_3 \quad (12.4)$$

where u, v , and w are integers. For cases where the lattice vectors are orthogonal, the basis vectors \mathbf{a}_1 , \mathbf{a}_2 , and \mathbf{a}_3 are assumed to be in the \hat{x} , \hat{y} , and \hat{z} directions. We have seen this notation before,⁷ for example, in the subscripts of the equations after definition 12.1.

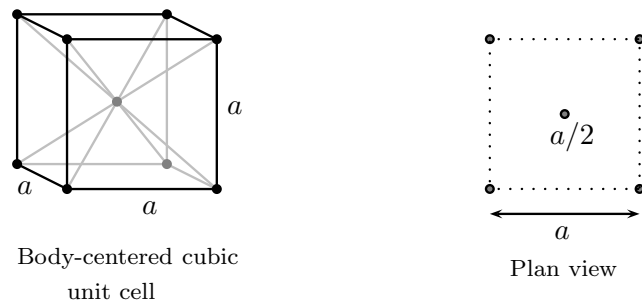
⁷This notation is also sometimes abused, as in Eq. 12.2 or Fig. 12.8, where the brackets enclose not integers, but distances. The notation can also be abused to specify points which are not members of the lattice, by choosing u , v , or w to be non-integers. We will sometimes engage in such abuse.

Lattices in three dimensions also exist where axes are not orthogonal. We will not cover all of these more complicated lattices in detail in this book. (In Section 12.2.4 we will briefly look through these other cases, but only at a very cursory level.) The principles we learn in the more simple cases (with orthogonal axes) generalize fairly easily, and just add further geometric and algebraic complexity without illuminating the physics much further.

Two particular lattices (with orthogonal axes) which we will cover in some detail are body-centered cubic (bcc) lattices and face-centered cubic (fcc) lattices.

12.2.1 The Body-Centered Cubic (bcc) Lattice

Fig. 12.12 Conventional unit cell for the body-centered cubic (I) lattice. **Left:** 3D view. **Right:** A plan view of the conventional unit cell. Unlabeled points are both at heights 0 and a .



The body-centered cubic (bcc) lattice is a simple cubic lattice where there is an additional lattice point in the very center of the cube (this is sometimes known⁸ as cubic-I.) The unit cell is shown in the left of Fig. 12.12. Another way to show this unit cell, which does not rely on showing a three-dimensional picture, is to use a so-called *plan view* of the unit cell, shown in the right of Fig. 12.12. A plan view (a term used in engineering and architecture) is a two-dimensional projection from the top of an object where heights are labeled to show the third dimension.

In the picture of the bcc unit cell, there are eight lattice points on the corners of the cell (each of which is $1/8$ inside of the conventional unit cell) and one point in the center of the cell. Thus the conventional unit cell contains exactly two ($= 8 \times 1/8 + 1$) lattice points.

⁸Cubic-I comes from “Innenzentriert” (inner-centered). This notation was introduced by Bravais in his 1848 treatise (Interestingly, Europe was burning in 1848, but obviously that didn’t stop science from progressing.)

Packing together these unit cells to fill space, we see that the lattice points of a full bcc lattice can be described as being points having coordinates $[x, y, z]$ where either all three coordinates are integers $[uvw]$ times the lattice constant a , or all three are half-odd-integers times the lattice constant a .

It is often convenient to think of the bcc lattice as a simple cubic lattice with a basis of two atoms per conventional cell. The simple cubic lattice contains points $[x, y, z]$ where all three coordinates are integers in units of the lattice constant. Within the conventional simple-cubic unit cell we put one point at position $[0, 0, 0]$ and another point at the position $[\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]$ in units of the lattice constant. Thus the points of the bcc lattice are written in units of the lattice constant as

$$\begin{aligned}\mathbf{R}_{\text{corner}} &= [n_1, n_2, n_3] \\ \mathbf{R}_{\text{center}} &= [n_1, n_2, n_3] + [\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]\end{aligned}$$

as if the two different types of points were two different types of atoms, although all points in this lattice should be considered equivalent (they only look inequivalent because we have chosen a conventional unit cell with two lattice points in it). From this representation we see that we can also think of the bcc lattice as being two interpenetrating simple cubic lattices displaced from each other by $[\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]$. (See also Fig. 12.14.)

We may ask why it is that this set of points forms a lattice. In terms of our first definition of a lattice (definition 12.1) we can write the primitive lattice vectors of the bcc lattice as

$$\begin{aligned}\mathbf{a}_1 &= [1, 0, 0] \\ \mathbf{a}_2 &= [0, 1, 0] \\ \mathbf{a}_3 &= [\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]\end{aligned}$$

in units of the lattice constant. It is easy to check that any combination

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3 \quad (12.5)$$

with n_1, n_2 , and n_3 integers gives a point within our definition of the bcc lattice (that the three coordinates are either all integers or all half-odd integers times the lattice constant). Further, one can check that any point satisfying the conditions for the bcc lattice can be written in the form of Eq. 12.5.

We can also check that our description of a bcc lattice satisfies our second description of a lattice (definition 12.1.1) that addition of any two points of the lattice (given by Eq. 12.5) gives another point of the lattice.

More qualitatively we can consider definition 12.1.2 of the lattice—that the local environment of every point in the lattice should be the same. Examining the point in the center of the unit cell, we see that it has precisely eight nearest neighbors in each of the possible diagonal directions. Similarly, any of the points in the corners of the unit cells will have eight nearest neighbors corresponding to the points in the center of the eight adjacent unit cells.

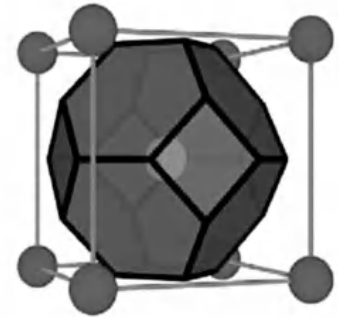


Fig. 12.13 The Wigner–Seitz cell of the bcc lattice (this shape is a “truncated octahedron”). The hexagonal face is the perpendicular bisecting plane between the lattice point (shown as a sphere) in the center and the lattice point (also a sphere) on the corner. The square face is the perpendicular bisecting plane between the lattice point in the center of the unit cell and a lattice point in the center of the neighboring unit cell.

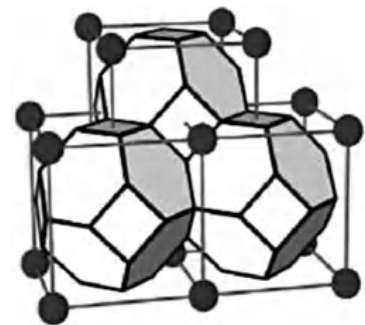


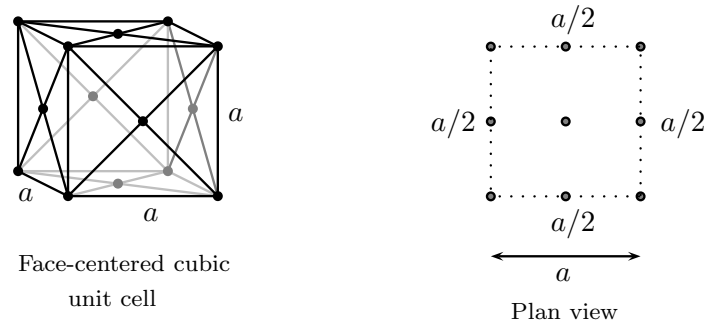
Fig. 12.14 The Wigner–Seitz cells of the bcc lattice pack together to tile all of space. Note that the structure of the bcc lattice is that of two interpenetrating simple cubic lattices.

The *coordination number* of a lattice (frequently called Z or z) is the number of nearest neighbors any point of the lattice has. For the bcc lattice the coordination number is $Z = 8$.

As in two dimensions, a Wigner–Seitz cell can be constructed around each lattice point which encloses all points in space that are closer to that lattice point than to any other point in the lattice. This Wigner–Seitz unit cell for the bcc lattice is shown in Fig. 12.13. Note that this cell is bounded by the perpendicular bisecting planes between lattice points. These Wigner–Seitz cells, being primitive, can be stacked together to fill all of space as shown in Fig. 12.14.

12.2.2 The Face-Centered Cubic (fcc) Lattice

Fig. 12.15 Conventional unit cell for the face-centered cubic (F) lattice. **Left:** 3D view. **Right:** A plan view of the conventional unit cell. Unlabeled points are both at heights 0 and a .



The face-centered (fcc) lattice is a simple cubic lattice where there is an additional lattice point in the center of every face of every cube (this is sometimes known as cubic-F, for “face-centered”). The unit cell is shown in the left of Fig. 12.15. A plan view of the unit cell is shown on the right of Fig. 12.15 with heights labeled to indicate the third dimension.

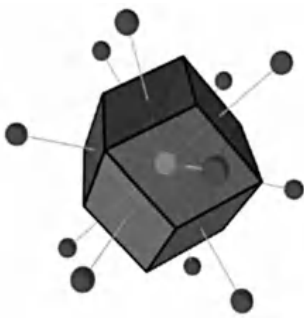


Fig. 12.16 The Wigner–Seitz cell of the fcc lattice (this shape is a “rhombic dodecahedron”). Each face is the perpendicular bisector between the central point and one of its 12 nearest neighbors.

In the picture of the fcc unit cell, there are eight lattice points on the corners of the cell (each of which is $1/8$ inside of the conventional unit cell) and one point in the center of each of the six faces (each of which is $1/2$ inside the cell). Thus the conventional unit cell contains exactly four ($= 8 \times 1/8 + 6 \times 1/2$) lattice points. Packing together these unit cells to fill space, we see that the lattice points of a full fcc lattice can be described as being points having coordinates (x, y, z) where either all three coordinates are integers times the lattice constant a , or two of the three coordinates are half-odd integers times the lattice constant a and the remaining one coordinate is an integer times the lattice constant a . Analogous to the bcc case, it is sometimes convenient to think of the fcc lattice as a simple cubic lattice with a basis of four atoms per conventional unit cell. The simple cubic lattice contains points $[x, y, z]$ where all three coordinates are integers in units of the lattice constant a . Within the conventional simple-cubic unit cell we put one point at position $[0, 0, 0]$ and another point at the position $[\frac{1}{2}, \frac{1}{2}, 0]$ another point

at $[\frac{1}{2}, 0, \frac{1}{2}]$ and another point at $[0, \frac{1}{2}, \frac{1}{2}]$. Thus the lattice points of the fcc lattice are written in units of the lattice constant as

$$\begin{aligned}\mathbf{R}_{corner} &= [n_1, n_2, n_3] \\ \mathbf{R}_{face-xy} &= [n_1, n_2, n_3] + [\frac{1}{2}, \frac{1}{2}, 0] \\ \mathbf{R}_{face-xz} &= [n_1, n_2, n_3] + [\frac{1}{2}, 0, \frac{1}{2}] \\ \mathbf{R}_{face-yz} &= [n_1, n_2, n_3] + [0, \frac{1}{2}, \frac{1}{2}].\end{aligned}\quad (12.6)$$

Again, this expresses the points of the lattice as if they were four different types of points but they only look inequivalent because we have chosen a conventional unit cell with four lattice points in it. Since the conventional unit cell has four lattice points in it, we can think of the fcc lattice as being four interpenetrating simple cubic lattices.

Again we can check that this set of points forms a lattice. In terms of our first definition of a lattice (definition 12.1) we write the primitive lattice vectors of the fcc lattice as

$$\begin{aligned}\mathbf{a}_1 &= [\frac{1}{2}, \frac{1}{2}, 0] \\ \mathbf{a}_2 &= [\frac{1}{2}, 0, \frac{1}{2}] \\ \mathbf{a}_3 &= [0, \frac{1}{2}, \frac{1}{2}]\end{aligned}$$

in units of the lattice constant. Again it is easy to check that any combination

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

with n_1, n_2 , and n_3 integers gives a point within our definition of the fcc lattice (that the three coordinates are either all integers, or two of three are half-odd integers and the remaining is an integer in units of the lattice constant a).

We can also similarly check that our description of a fcc lattice satisfies our other two definitions of (definition 12.1.1 and 12.1.2) of a lattice. The Wigner–Seitz unit cell for the fcc lattice is shown in Fig. 12.16. In Fig. 12.17 it is shown how these Wigner–Seitz cells pack together to fill all of space.

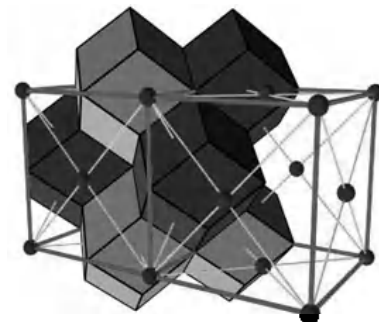


Fig. 12.17 The Wigner–Seitz cells of the fcc lattice pack together to tile all of space. Also shown in the picture are two conventional (cubic) unit cells.

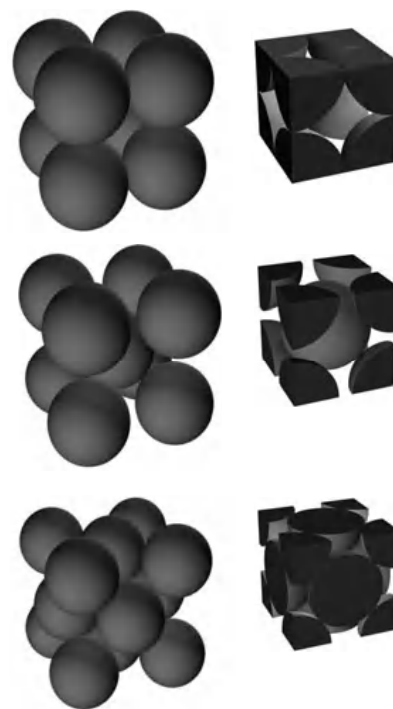


Fig. 12.18 **Top:** Simple cubic, **Middle:** bcc, **Bottom:** fcc. The left shows packing of spheres into these lattices. The right shows a cutaway of the conventional unit cell exposing how the fcc and bcc lattices leave much less empty space than the simple cubic.

12.2.3 Sphere Packing

Although the simple cubic lattice (see Fig. 12.10) is conceptually the simplest of all lattices, in fact, real crystals of atoms are rarely simple cubic.⁹ To understand why this is so, think of atoms as small spheres that weakly attract each other and therefore try to pack close together. When you assemble spheres into a simple cubic lattice you find that it is a very inefficient way to pack the spheres together—you are left with a lot of empty space in the center of the unit cells, and this turns out to be energetically unfavorable in most cases. Packings of spheres into simple cubic, bcc, and fcc lattices are shown in Fig. 12.18. It is easy to see that the bcc and fcc lattices leave much less open space between

⁹Of all of the chemical elements, polonium is the only one which can form a simple cubic lattice with a single atom basis. (It can also form another crystal structure depending on how it is prepared.)

¹⁰In fact it is impossible to pack spheres more densely than you would get by placing the spheres at the vertices of an fcc lattice. This result (known empirically to people who have tried to pack oranges in a crate) was first officially conjectured by Johannes Kepler in 1611, but was not mathematically proven until 1998! Note however that there is another lattice, the *hexagonal close packed* lattice which achieves precisely the same packing density for spheres as the fcc lattice.

the spheres than packing the spheres in a simple cubic lattice¹⁰ (see also Exercise 12.4). Correspondingly, bcc and fcc lattices are realized much more frequently in nature than simple cubic (at least in the case of a single atom basis). For example, the elements Al, Ca, Au, Pb, Ni, Cu, Ag (and many others) are fcc whereas the elements Li, Na, K, Fe, Mo, Cs (and many others) are bcc.

12.2.4 Other Lattices in Three Dimensions

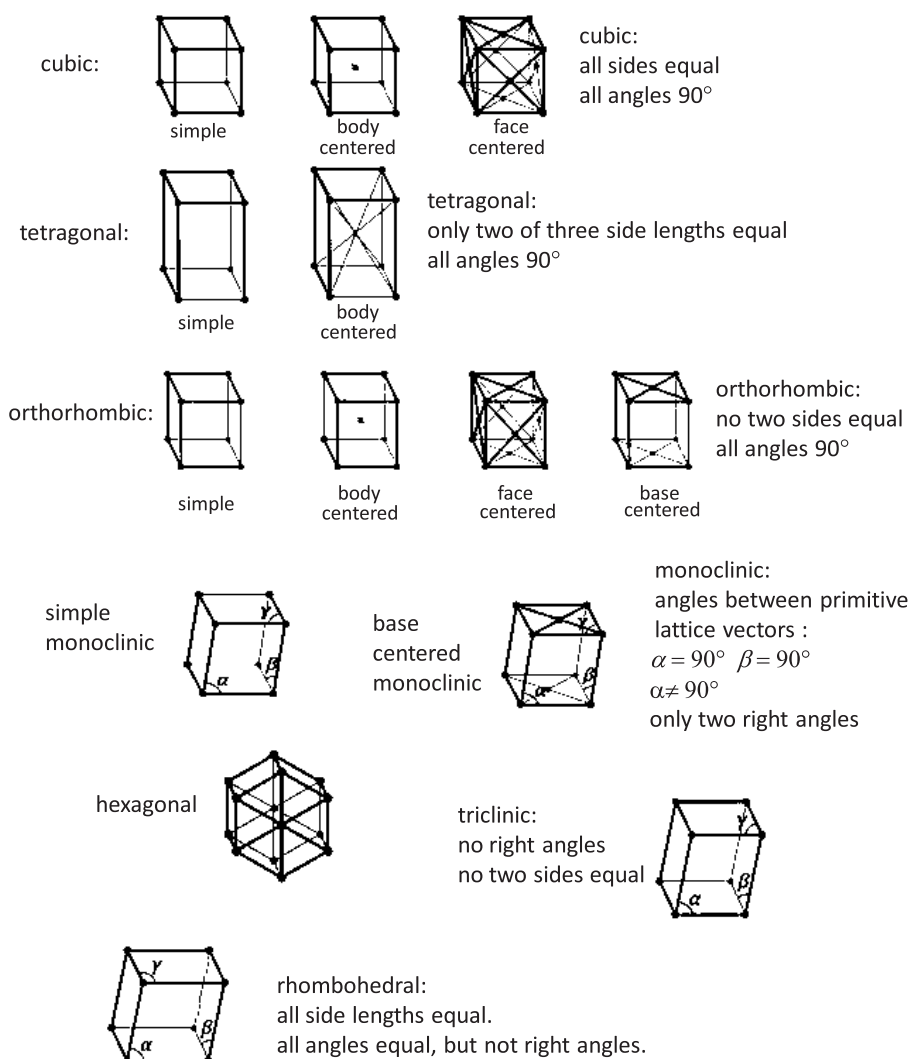


Fig. 12.19 Conventional unit cells for the fourteen Bravais lattice types. Note that if you tried to construct a “face-centered tetragonal” lattice, you would find that by turning the axes at 45 degrees it would actually be equivalent to a body-centered tetragonal lattice. Hence face-centered tetragonal is not listed as a Bravais lattice type (nor is base-centered tetragonal for a similar reason, etc.).

¹¹Named after Auguste Bravais who classified all the three-dimensional lattices in 1848. Actually they should be named after Moritz Frankenheim who studied the same thing over ten years earlier—although he made a minor error in his studies, and therefore missed getting his name associated with them.

In addition to the simple cubic, orthorhombic, tetragonal, fcc, and bcc lattices, there are nine other types of lattices in three dimensions. These are known as the fourteen *Bravais lattice types*.¹¹ Although the study of all of these lattice types is beyond the scope of this book, it is probably a good idea to know that they exist.

Figure 12.19 shows the full variety of Bravais lattice types in three di-


mensions. While it is an extremely deep fact that there are only fourteen lattice types in three dimensions, the precise statement of this theorem, as well of the proof of it, are beyond the scope of this book. The key result is that any crystal, no matter how complicated, has a lattice which is one of these fourteen types.¹²

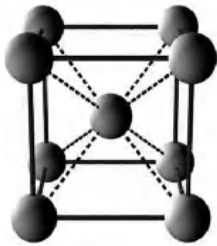
12.2.5 Some Real Crystals

Once we have discussed lattices we can combine a lattice with a basis to describe any periodic structure—and in particular, we can describe any crystalline structure. Several examples of real (and reasonably simple) crystal structures are shown in Figs. 12.20 and 12.21.

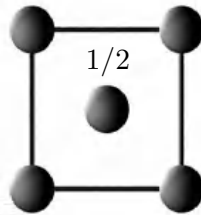
Sodium (Na)

Lattice = Cubic-I (bcc)

Basis = Na at $[000]$ 





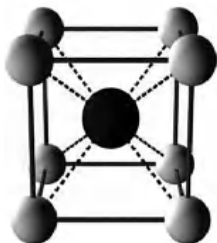
Plan view
unlabeled points at $z = 0, 1$



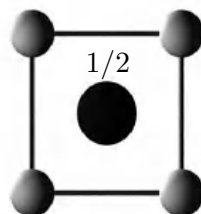
Caesium chloride (CsCl)

Lattice = Cubic-P 

Basis = Cs at $[000]$ 
and Cl at $[\frac{1}{2}\frac{1}{2}\frac{1}{2}]$ 




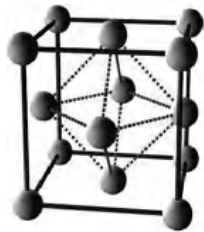
Plan view
unlabeled points at $z = 0, 1$



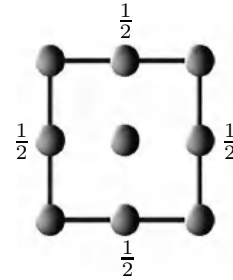
¹²There is a real subtlety here in classifying a crystal as having a particular lattice type. There are only these fourteen lattice types, but in principle a crystal could have one lattice, but have the *symmetry* of another lattice. An example of this would be if the a lattice were cubic, but the unit cell did not look the same from all six sides. Crystallographers would not classify this as being a cubic material even if the lattice happened to be cubic. The reason for this is that if the unit cell did not look the same from all six sides, there would be no particular reason that the three primitive lattice vectors should have the same length—it would be an insane coincidence were this to happen, and almost certainly in any real material the primitive lattice vector lengths would actually have slightly different values if measured more closely.

Fig. 12.20 Top: Sodium forms a bcc lattice. **Bottom:** Caesium chloride forms a cubic lattice with a two atom basis. Note carefully: CsCl is *not* bcc! In a bcc lattice all of the points (including the body center) must be identical. For CsCl, the point in the center is Cl whereas the points in the corner are Cs.

Copper(Cu)
 Lattice = Cubic-F (fcc)
 Basis = Cu at $[000]$ 



Plan view
 unlabeled points at $z = 0, 1$




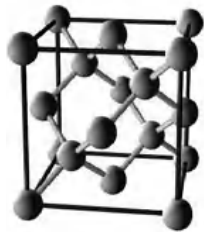
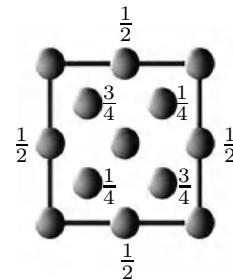


Diamond (C); also Si and Ge
 Lattice = Cubic-F (fcc)
 Basis = C at $[000]$
 and C at $[\frac{1}{4}\frac{1}{4}\frac{1}{4}]$ 

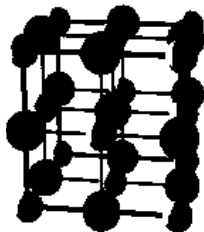
Fig. 12.21 Some crystals based on the fcc lattice. **Top:** Copper forms an fcc lattice. **Middle:** Diamond (carbon) is an fcc lattice with a two-atom basis. **Bottom:** NaCl (salt) is also an fcc lattice with a two atom basis. Note that in every case, a conventional unit cell is shown but the basis is given for the primitive unit cell.



Plan view
 unlabeled points at $z = 0, 1$



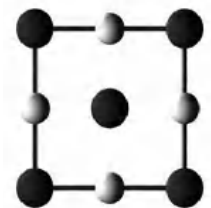
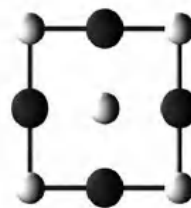
Sodium Chloride (NaCl)
 Lattice = Cubic-F (fcc)
 Basis = Na at $[000]$ 
 and Cl at $[\frac{1}{2}\frac{1}{2}\frac{1}{2}]$ 



Plan view

$z = 0, 1$ layer

$z = \frac{1}{2}$ layer



Chapter summary

This chapter introduced a plethora of new definitions, aimed at describing crystal structure in three dimensions. Here is a list of some of the concepts that one should know:

- Definition of a *lattice* in three different ways. See definitions 12.1, 12.1.1, 12.1.2.
- Definition of a *unit cell* for a periodic structure, and definition of a *primitive unit cell* and a *conventional unit cell*.
- Definition and construction of the *Wigner–Seitz (primitive) unit cell*.
- One can write any periodic structure in terms of a lattice and a basis (see examples in Fig. 12.20 and 12.21).
- In 3d, know the simple cubic lattice, the fcc lattice and the bcc lattices in particular. Orthorhombic and tetragonal lattices are also very useful to know.
- The fcc and bcc lattices can be thought of as simple cubic lattices with a basis.
- Know how to read a *plan view* of a structure.

References

All solid state books cover crystal. Some books give *way* too much detail. I recommend the following as giving not too much and not too little:

- Kittel, chapter 1
- Ashcroft and Mermin, chapter 4 (Caution of the nomenclature issue, see margin note 1 of this chapter.)
- Hook and Hall, sections 1.1–1.3 (probably not enough detail here!)

For greater detail about crystal structure see the following:

- Glazer, chapters 1–3
- Dove, sections 3.1–3.2 (brief but good)

Exercises

(12.1) Crystal Structure of NaCl

Consider the NaCl crystal structure shown in Fig. 12.21. If the lattice constant is $a = 0.563$ nm, what is the distance from a sodium atom to the nearest chlorine? What is the distance from a sodium atom to the nearest other sodium atom?

(12.2) Neighbors in the Face-Centered Lattice.

- (a) Show that each lattice point in an fcc lattice has twelve nearest neighbors, each the same distance from the initial point. What is this distance if the conventional unit cell has lattice constant a ?
- (b)* Now stretch the side lengths of the fcc lattice

such that you obtain a face-centered *orthorhombic* lattice where the conventional unit cell has sides of length a , b , and c which are all different. What are the distances to these twelve neighboring points now? How many nearest neighbors are there?

(12.3) **Crystal Structure**

The diagram of Fig. 12.22 shows a plan view of a structure of cubic ZnS (zincblende) looking down the z axis. The numbers attached to some atoms represent the heights of the atoms above the $z = 0$ plane expressed as a fraction of the cube edge a . Unlabeled atoms are at $z = 0$ and $z = a$.

- (a) What is the Bravais lattice type?
- (b) Describe the basis.
- (c) Given that $a = 0.541$ nm, calculate the nearest-neighbor Zn–Zn, Zn–S, and S–S distances.

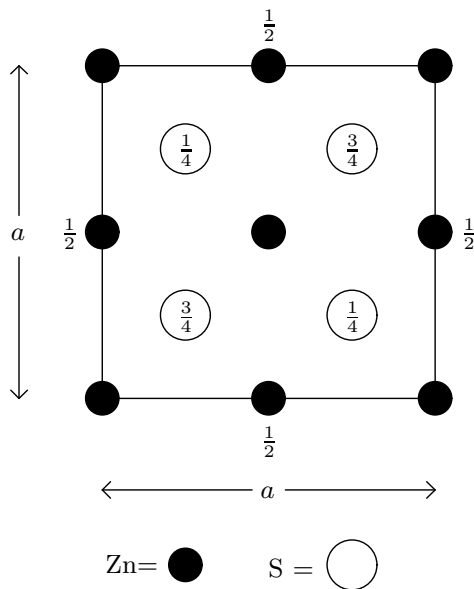


Fig. 12.22 Plan view of conventional unit cell of zincblende.

(12.4) **Packing Fractions**

Consider a lattice with a sphere at each lattice point. Choose the radius of the spheres to be such that neighboring spheres just touch (see for example, Fig. 12.18). The packing fraction is the fraction of the volume of all of space which is enclosed by the union of all the spheres (i.e., the ratio of the volume of the spheres to the total volume).

- (a) Calculate the packing fraction for a simple cubic lattice.
- (b) Calculate the packing fraction for a bcc lattice.
- (c) Calculate the packing fraction for an fcc lattice.

(12.5) **Fluorine Beta Phase**

Fluorine can crystallize into a so-called beta-phase at temperatures between 45 and 55 Kelvin. Fig. 12.23 shows the cubic conventional unit cell for beta phase fluorine in three-dimensional form along with a plan view.

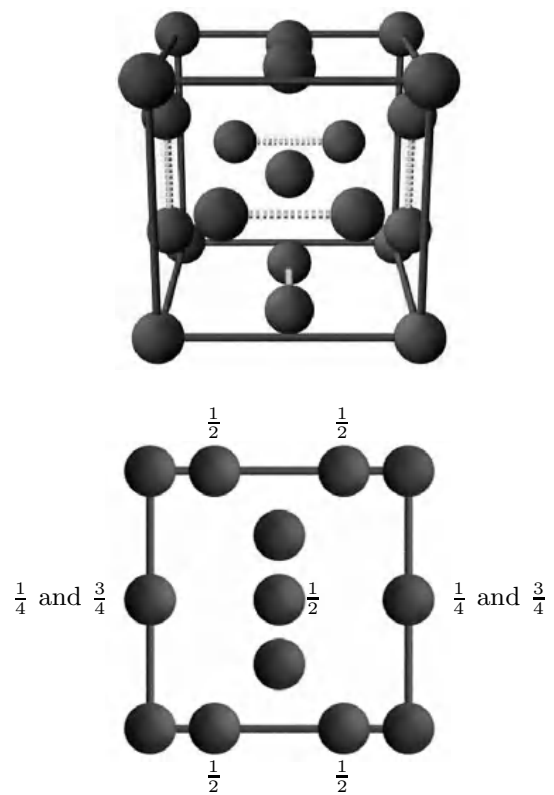


Fig. 12.23. A conventional unit cell for fluorine beta phase. All atoms in the picture are fluorine. Lines are drawn for clarity **Top:** Three-dimensional view. **Bottom:** Plan view. Unlabeled atoms are at height 0 and 1 in units of the lattice constant.

- ▷ How many atoms are in this conventional unit cell?
- ▷ What is the lattice and the basis for this crystal?

Reciprocal Lattice, Brillouin Zone, Waves in Crystals

13

In the last chapter we explored lattices and crystal structure. However, as we saw in Chapters 9–11, the important physics of waves in solids (whether they are vibrational waves, or electron waves) is best described in reciprocal space. This chapter thus introduces reciprocal space in three dimensions. As with the previous chapter, there is some tricky geometry in this chapter, and a few definitions to learn as well. As a result this material is a bit tough to slog through, but stick with it because soon we will make substantial use of what we learn here. At the end of this chapter we will finally have enough definitions to describe the dispersions of phonons and electrons in three-dimensional systems.

13.1 The Reciprocal Lattice in Three Dimensions

13.1.1 Review of One Dimension

Let us first recall some results from our study of one dimension. We consider a simple lattice in one dimension $R_n = na$ with n an integer. Recall that two points in k -space (reciprocal space) were defined to be equivalent to each other if $k_1 = k_2 + G_m$ where $G_m = 2\pi m/a$ with m an integer. The points G_m form the reciprocal lattice.

Recall that the reason that we identified different k values with each other was because we were considering waves of the form

$$e^{ikx_n} = e^{ikna}$$

with n an integer. Because of this form of the wave, we find that shifting $k \rightarrow k + G_m$ leaves this functional form unchanged since

$$e^{i(k+G_m)x_n} = e^{i(k+G_m)na} = e^{ikna} e^{i(2\pi m/a)na} = e^{ikx_n}$$

where we have used

$$e^{i2\pi mn} = 1$$

in the last step. Thus, so far as the wave is concerned, k is the same as $k + G_m$.

13.1.2 Reciprocal Lattice Definition

Generalizing this one-dimensional result, we define

Definition 13.1 *Given a (direct) lattice of points \mathbf{R} , a point \mathbf{G} is a point in the reciprocal lattice if and only if*

$$e^{i\mathbf{G}\cdot\mathbf{R}} = 1 \quad (13.1)$$

for all points \mathbf{R} of the direct lattice.

To construct the reciprocal lattice, let us first write the points of the direct lattice in the form¹ (here we specialize to the three-dimensional case)

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3 \quad (13.2)$$

with n_1, n_2 , and n_3 integers, and with \mathbf{a}_1 , \mathbf{a}_2 , and \mathbf{a}_3 being primitive lattice vectors of the direct lattice.

We now make two key claims:

- (1) We claim that the reciprocal lattice (defined by Eq. 13.1) is a lattice in reciprocal space (thus explaining its name).
- (2) We claim that the primitive lattice vectors of the reciprocal lattice (which we will call \mathbf{b}_1 , \mathbf{b}_2 , and \mathbf{b}_3) are defined to have the following property:

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij} \quad (13.3)$$

where δ_{ij} is the Kronecker delta.²

We can certainly construct vectors \mathbf{b}_i to have the desired property of Eq. 13.3, as follows:

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

It is easy to check that Eq. 13.3 is satisfied. For example,

$$\begin{aligned} \mathbf{a}_1 \cdot \mathbf{b}_1 &= \frac{2\pi \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} = 2\pi \\ \mathbf{a}_2 \cdot \mathbf{b}_1 &= \frac{2\pi \mathbf{a}_2 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} = 0. \end{aligned}$$

Now, given vectors \mathbf{b}_1 , \mathbf{b}_2 , and \mathbf{b}_3 satisfying Eq. 13.3 we have claimed that these are in fact primitive lattice vectors for the reciprocal lattice. To prove this, let us write an *arbitrary* point in reciprocal space as

$$\mathbf{G} = m_1\mathbf{b}_1 + m_2\mathbf{b}_2 + m_3\mathbf{b}_3 \quad (13.4)$$

¹There are certainly other ways to specify the points of a direct lattice. For example, it is sometimes convenient to choose \mathbf{a}_i 's to describe the edges vectors of a *conventional* unit cell, but then the n_i 's are not simply described as all integers. This is done in section 13.1.5, and is relevant for the **Important Comment** there.

²Leopold Kronecker was a mathematician who is famous (among other things) for the sentence "God made the integers, everything else is the work of man". In case you don't already know this, the Kronecker delta is defined as $\delta_{ij} = 1$ for $i = j$ and is zero otherwise. (Kronecker did a lot of other interesting things as well.)

and for the moment, let us not require m_1, m_2 , and m_3 to be integers. (We are about to discover that for \mathbf{G} to be a point of the reciprocal lattice, they must be integers, but this is what we want to prove!)

To find points of the reciprocal lattice we must show that Eq. 13.1 is satisfied for all points $\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$ of the direct lattice with n_1, n_2 , and n_3 integers. We thus write

$$e^{i\mathbf{G}\cdot\mathbf{R}} = e^{i(m_1\mathbf{b}_1+m_2\mathbf{b}_2+m_3\mathbf{b}_3)\cdot(n_1\mathbf{a}_1+n_2\mathbf{a}_2+n_3\mathbf{a}_3)} = e^{2\pi i(n_1m_1+n_2m_2+n_3m_3)}$$

In order for \mathbf{G} to be a point of the reciprocal lattice, this must equal unity for all points \mathbf{R} of the direct lattice, i.e., for all integer values of n_1, n_2 and n_3 . Clearly this can only be true if m_1, m_2 and m_3 are also integers. Thus, we find that the points of the reciprocal lattice are precisely those of the form of Eq. 13.4 with m_1, m_2 and m_3 integers. This further proves our claim that the reciprocal lattice is in fact a lattice!

13.1.3 The Reciprocal Lattice as a Fourier Transform

Quite generally one can think of the reciprocal lattice as being a Fourier transform of the direct lattice. It is easiest to start by thinking in one dimension. Here the direct lattice is given again by $R_n = an$. If we want to describe a “density” of lattice points in one dimension, we might put a delta function at each lattice points and write the density as³

$$\rho(r) = \sum_n \delta(r - an).$$

Fourier transforming this function gives⁴

$$\begin{aligned} \mathcal{F}[\rho(r)] &= \int dr e^{ikr} \rho(r) = \sum_n \int dr e^{ikr} \delta(r - an) = \sum_n e^{ikan} \\ &= \frac{2\pi}{|a|} \sum_m \delta(k - 2\pi m/a). \end{aligned}$$

The last step here is a bit non-trivial.⁵ Here e^{ikan} is clearly unity if $k = 2\pi m/a$, i.e., if k is a point on the reciprocal lattice. In this case, each term of the sum contributes unity to the sum and one obtains an infinite result.⁶ If k is not such a reciprocal lattice point, then the terms of the sum oscillate and the sum comes out to be zero.

This principle generalizes to the higher (two- and three-)dimensional cases. Generally

$$\mathcal{F}[\rho(\mathbf{r})] = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} = \frac{(2\pi)^D}{v} \sum_{\mathbf{G}} \delta^D(\mathbf{k} - \mathbf{G}) \quad (13.5)$$

where in the middle term, the sum is over lattice points \mathbf{R} of the direct lattice, and in the last term it is a sum over points \mathbf{G} of the reciprocal lattice and v is the volume of the unit cell. Here D is the number of dimensions (1, 2 or 3) and the δ^D is a D -dimensional delta function.⁷

³Since the sums are over all lattice points they should go from $-\infty$ to $+\infty$. Alternatively, one uses periodic boundary conditions and sums over all points.

⁴With Fourier transforms there are several different conventions about where one puts the factors of 2π . Possibly in your mathematics class you learned to put $1/\sqrt{2\pi}$ with each integral. However, in solid state physics, conventionally $1/(2\pi)$ comes with each k integral, and no factor of 2π comes with each r integral. See Section 2.2.1 to see why this is used.

⁵This is sometimes known as the Poisson resummation formula, after Siméon Denis Poisson, the same guy after whom Poisson’s equation $\nabla^2\phi = -\rho/\epsilon_0$ is named, as well as other mathematical things such as the Poisson random distribution. His last name means “fish” in French.

⁶Getting the prefactor right is a bit harder. But actually, the prefactor isn’t going to be too important for us.

⁷For example, in two dimensions $\delta^2(\mathbf{r} - \mathbf{r}_0) = \delta(x - x_0)\delta(y - y_0)$ where $\mathbf{r} = (x, y)$

The equality in Eq. 13.5 is similar to the one-dimensional case. If \mathbf{k} is a point of the reciprocal lattice, then $e^{i\mathbf{k}\cdot\mathbf{R}}$ is always unity and the sum is infinite. However, if \mathbf{k} is not a point on the reciprocal lattice then the summands oscillate, and the sum comes out to be zero. Thus one obtains delta-function peaks precisely at the positions of reciprocal lattice vectors.

⁸See Exercise 13.1.

Aside: It is an easy exercise to show⁸ that the reciprocal lattice of an fcc direct lattice is a bcc lattice in reciprocal space. Conversely, the reciprocal lattice of a bcc direct lattice is an fcc lattice in reciprocal space.

Fourier Transform of Any Periodic Function

In the prior section we considered the Fourier transform of a function $\rho(\mathbf{r})$ which is just a set of delta functions at lattice points. However, it is not too different to consider the Fourier transform of *any* function with the periodicity of the lattice (and this will be quite important in Chapter 14). We say a function $\rho(\mathbf{r})$ has the periodicity of a lattice if $\rho(\mathbf{r}) = \rho(\mathbf{r} + \mathbf{R})$ for any lattice vector \mathbf{R} . We then want to calculate

$$\mathcal{F}[\rho(\mathbf{r})] = \int d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} \rho(\mathbf{r}).$$

The integral over all of space can be broken up into a sum of integrals over each unit cell. Here we write any point in space \mathbf{r} as the sum of a lattice point \mathbf{R} and a vector \mathbf{x} within the unit cell

$$\mathcal{F}[\rho(\mathbf{r})] = \sum_{\mathbf{R}} \int_{unit-cell} d\mathbf{x} e^{i\mathbf{k}\cdot(\mathbf{x}+\mathbf{R})} \rho(\mathbf{x} + \mathbf{R}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \int_{unit-cell} d\mathbf{x} e^{i\mathbf{k}\cdot\mathbf{x}} \rho(\mathbf{x}).$$

where here we have used the invariance of ρ under lattice translations $\mathbf{x} \rightarrow \mathbf{x} + \mathbf{R}$. The sum of exponentials, as in Eq. 13.5, just gives a sum of delta functions yielding

$$\mathcal{F}[\rho(\mathbf{r})] = (2\pi)^D \sum_{\mathbf{G}} \delta^D(\mathbf{k} - \mathbf{G}) S(\mathbf{k})$$

where

$$S(\mathbf{k}) = \int_{unit-cell} d\mathbf{x} e^{i\mathbf{k}\cdot\mathbf{x}} \rho(\mathbf{x}) \quad (13.6)$$

is known as the *structure factor* and will become very important in the next chapter.

13.1.4 Reciprocal Lattice Points as Families of Lattice Planes

Another way to understand the reciprocal lattice is via families of lattice planes of the direct lattice.

Definition 13.2 A *lattice plane* (or *crystal plane*) is a plane containing at least three non-collinear (and therefore an infinite number of) points of a lattice.

Definition 13.3 A *family of lattice planes* is an infinite set of equally separated parallel lattice planes which taken together contain all points of the lattice.

In Fig. 13.1, several examples of families of lattice planes are shown. Note that the planes are parallel and equally spaced, and every point of the lattice is included in exactly one lattice plane.

I now make the following claim:

Claim 13.1 The families of lattice planes are in one-to-one correspondence⁹ with the possible directions of reciprocal lattice vectors, to which they are normal. Further, the spacing between these lattice planes is $d = 2\pi/|\mathbf{G}_{\min}|$ where \mathbf{G}_{\min} is the minimum length reciprocal lattice vector in this normal direction.

This correspondence is made as follows. First we consider the set of planes defined by points \mathbf{r} such that for some integer m ,

$$\mathbf{G} \cdot \mathbf{r} = 2\pi m. \quad (13.7)$$

This defines an infinite set of parallel planes normal to \mathbf{G} . Since $e^{i\mathbf{G} \cdot \mathbf{r}} = 1$ we know that every lattice point is a member of one of these planes (since this is the definition of \mathbf{G} in Eq. 13.1). However, for the planes defined by Eq. 13.7, not every plane needs to contain a lattice point (so generically this is a family of parallel equally spaced planes, but not a family of lattice planes). For this larger family of planes, the spacing between planes is given by

$$d = \frac{2\pi}{|\mathbf{G}|}. \quad (13.8)$$

To prove this we simply note (from Eq. 13.7) that two adjacent planes must have

$$\mathbf{G} \cdot (\mathbf{r}_1 - \mathbf{r}_2) = 2\pi.$$

Thus in the direction parallel to \mathbf{G} , the spacing between planes is $2\pi/|\mathbf{G}|$ as claimed.

Clearly different values of \mathbf{G} that happen to point in the same direction, but have different magnitudes, will define parallel sets of planes. As we increase the magnitude of \mathbf{G} , we add more and more planes. For example, examining Eq. 13.7 we see that when we double the magnitude of \mathbf{G} we correspondingly double the density of planes, which we can see from the spacing formula Eq. 13.8. However, whichever \mathbf{G} we choose, all of the lattice points will be included in one of the defined planes. If we choose the maximally possible spaced planes, hence the smallest possible value of \mathbf{G} allowed in any given direction which we call \mathbf{G}_{\min} , then in fact every defined plane will include lattice points and therefore be

⁹For this one-to-one correspondence to be precisely true we must define \mathbf{G} and $-\mathbf{G}$ to be the same direction. If this sounds like a cheap excuse, we can say that “oriented” families of lattice planes are in one-to-one correspondence with the directions of reciprocal lattice vectors, thus keeping track of the two possible normals of the family of lattice planes.

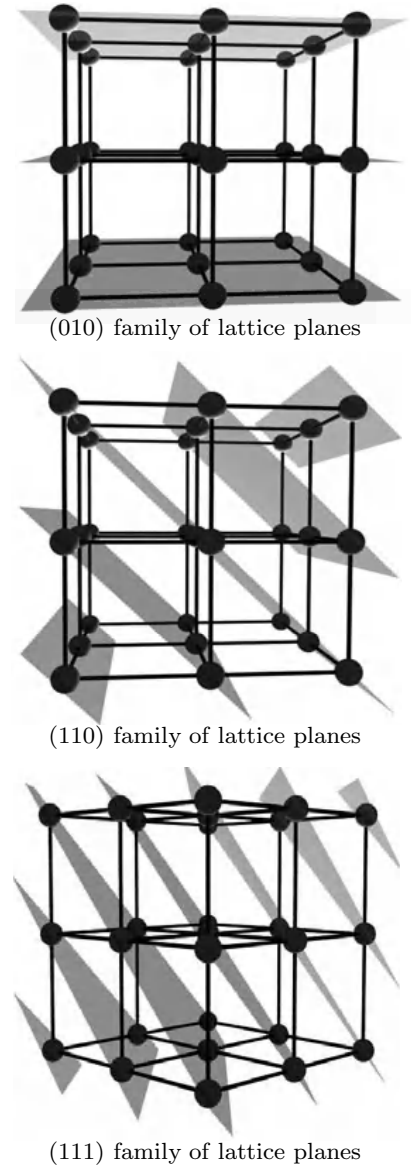


Fig. 13.1 Examples of families of lattice planes on the cubic lattice. Each of these planes is a lattice plane because it intersects at least three non-collinear lattice points. Each picture is a family of lattice planes since every lattice point is included in one of the parallel lattice planes. The families are labeled in Miller index notation. **Top** (010); **Middle** (110); **Bottom** (111). In the top and middle the x -axis points to the right and the y -axis points up. In the bottom figure the axes are rotated for clarity.

lattice planes, and the spacing between these planes is correspondingly $2\pi/|\mathbf{G}_{\min}|$. This proves¹⁰ Claim 13.1.

13.1.5 Lattice Planes and Miller Indices

There is a useful notation for describing lattice planes (or reciprocal lattice vectors) known as *Miller indices*.¹¹ One first chooses edge vectors \mathbf{a}_i for a unit cell in direct space (which may be primitive or non-primitive). One then constructs reciprocal space vectors \mathbf{b}_i to satisfy $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$ (see Eq. 13.3). In terms of these vectors \mathbf{b}_i , one writes (h, k, l) or (hkl) with integers h, k and l , to mean the reciprocal space vector¹²

$$\mathbf{G}_{(h,k,l)} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3. \quad (13.9)$$

Note that Miller indices can be negative, such as $(1, -1, 1)$. Conventionally, the minus sign is denoted with an over-bar rather than a minus sign, so we write $(1\bar{1}1)$ instead.¹³

Note that if one chooses \mathbf{a}_i to be the real (direct) space primitive lattice vectors, then \mathbf{b}_i will be the primitive lattice vectors for the reciprocal lattice. In this case, any set of integer Miller indices (hkl) represents a reciprocal lattice vector. To represent a family of lattice plane, one should take the shortest reciprocal lattice vector in the given direction (see Claim 13.1), meaning h, k , and l should have no common divisors. If (hkl) are not the shortest reciprocal lattice vector in a given direction, then they represent a family of planes that is not a family of lattice planes (i.e., there are some planes that do not intersect lattice points).

On the other hand, if one chooses \mathbf{a}_i to describe the edges of some non-primitive (conventional) unit cell, the corresponding \mathbf{b}_i will not be primitive reciprocal lattice vectors. As a result not all integer sets of Miller indices will be reciprocal lattice vectors.

Important Comment: For any cubic lattice (simple cubic, fcc, or bcc) it is conventional to choose \mathbf{a}_i to be $a\hat{x}, a\hat{y}$, and $a\hat{z}$ with a the cube edge length. I.e., one chooses the orthogonal edge vectors of the conventional (cube) unit cell. Correspondingly, \mathbf{b}_i are the vectors $2\pi\hat{x}/a, 2\pi\hat{y}/a$, and $2\pi\hat{z}/a$. For the primitive (simple) cubic case these are primitive reciprocal lattice vectors, but for the fcc and bcc case, they are not.¹⁴ So in the fcc and bcc cases not all integer sets of Miller indices (hkl) are reciprocal lattice vectors.

To illustrate this point, consider the (010) family of planes for the cubic lattice, shown in the top of Fig. 13.1. This family of planes intersects every corner of the cubic unit cell. However, if we were discussing a bcc lattice, there would also be another lattice point in the center of every conventional unit cell which the (010) lattice planes would not intersect (see top of Fig. 13.2). However, the (020) planes *would* intersect these

¹¹These are named after the nineteenth century mineralogist William Hallowes Miller.

¹²We have already used the corresponding notation $[uvw]$ to represent lattice points of the direct lattice. See for example, Eq. 12.1 and Eq. 12.4.

¹³How $(1\bar{1}1)$ is pronounced is a bit random. Some people say “one-(bar-one)-one” and others say “one-(one-bar)-one”. I have no idea how the community got so confused as to have these two different conventions. I think in Europe the former is more prevalent whereas in America the latter is more prevalent. At any rate, it is always clear when it is written.

¹⁴Although this convention of working with non-primitive vectors \mathbf{b}_i makes some things very complicated our only other option would be to work with the non-orthogonal coordinate axes of the primitive lattice vectors—which would complicate life even more!

¹⁰More rigorously, if there is a family of lattice planes in direction $\hat{\mathbf{G}}$ with spacing between planes d , then $\mathbf{G} = 2\pi\hat{\mathbf{G}}/d$ is necessarily a reciprocal lattice vector. To see this note that $e^{i\mathbf{G}\cdot\mathbf{R}} = 1$ will be unity for all lattice points. Further, in a family of lattice planes, all lattice points are included within the planes, so $e^{i\mathbf{G}\cdot\mathbf{R}} = 1$ for all \mathbf{R} a lattice point, which implies \mathbf{G} is a reciprocal lattice vector. Furthermore, \mathbf{G} is the shortest reciprocal lattice vector in the direction of $\hat{\mathbf{G}}$ since increasing \mathbf{G} will result in a smaller spacing of lattice planes and some planes will not intersect lattice points \mathbf{R} .

central points as well, so in this case (020) represents a true family of lattice planes (and hence a reciprocal lattice vector) for the bcc lattice whereas (010) does not! (See Fig. 13.2.) In Section 14.2 we will discuss the “selection rules” for knowing when a set of Miller indices represents a true family of lattice planes in the fcc and bcc cases.

From Eq. 13.8 one can write the spacing between adjacent planes of a family of planes specified by Miller indices (h, k, l)

$$d_{(hkl)} = \frac{2\pi}{|\mathbf{G}|} = \frac{2\pi}{\sqrt{h^2|\mathbf{b}_1|^2 + k^2|\mathbf{b}_2|^2 + l^2|\mathbf{b}_3|^2}} \quad (13.10)$$

where we have assumed that the coordinate axes of the lattice vectors \mathbf{b}_i are orthogonal. Recall that in the case of orthogonal axes $|b_i| = 2\pi/|a_i|$ where a_i are the lattice constants in the three orthogonal directions. Thus we can equivalently write

$$\frac{1}{|d_{(hkl)}|^2} = \frac{h^2}{a_1^2} + \frac{k^2}{a_2^2} + \frac{l^2}{a_3^2}. \quad (13.11)$$

Note that for a cubic lattice this simplifies to

$$d_{(hkl)}^{cubic} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}. \quad (13.12)$$

A useful shortcut for figuring out the geometry of lattice planes is to look at the intersection of a plane with the three coordinate axes. The intersections x_1, x_2, x_3 with the three coordinate axes (in units of the three lattice constants) are related to the Miller indices via

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

This construction is illustrated in Fig. 13.3.

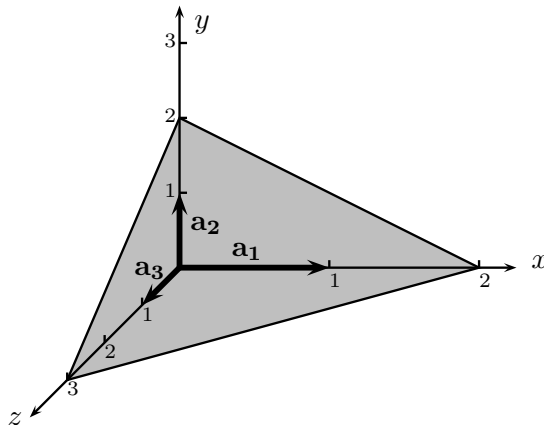
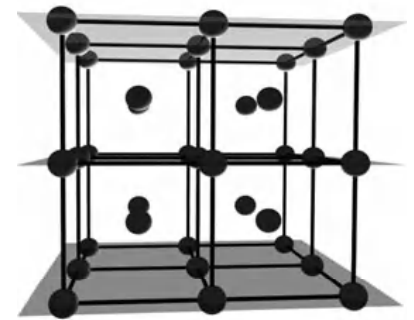
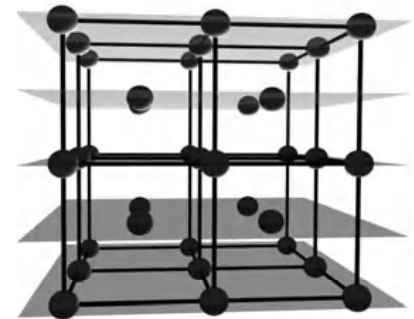


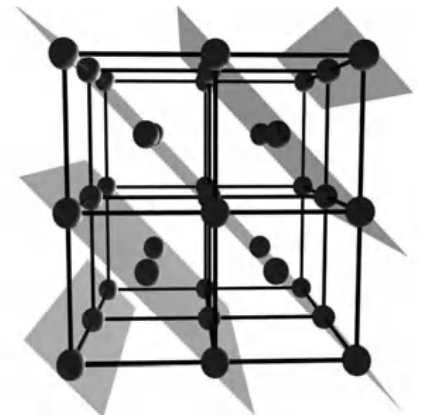
Fig. 13.3 Determining Miller indices from the intersection of a plane with the coordinate axes. This plane intersects the coordinate axes at $x = 2$, $y = 2$ and $z = 3$ in units of the lattice constants. The reciprocals of these intercepts are $\frac{1}{2}, \frac{1}{2}, \frac{1}{3}$. The smallest integers having these ratios are 3, 3, 2. Thus the Miller indices of this family of lattice planes are (332). The spacing between lattice planes in this family would be $1/|d_{(233)}|^2 = 3^2/a_1^2 + 3^2/a_2^2 + 2^2/a_3^2$ (assuming orthogonal axes).



(010) family of planes
(not all lattice points included)



(020) family of lattice planes



(110) family of planes

Fig. 13.2 Top: For the bcc lattice, the (010) planes are not a true family of lattice planes since the (010) planes do not intersect the lattice points in the middle of the cubes. **Middle:** The (020) planes are a family of lattice planes since they intersect all of the lattice points. **Bottom** The (110) planes are also a family of lattice planes.

¹⁵It can sometimes be subtle to figure out if a crystal looks the same from two different directions: one needs to check that the *basis* of the crystal looks the same from the two directions!

¹⁶There is a law known as “Bravais’ law”, which states that crystals cleave most readily along faces having the highest density of lattice points, or equivalently the largest distance between lattice planes. To a large extent this means that crystals cleave on lattice planes with small Miller indices.

Finally, we note that different lattice planes may be the same under a symmetry of the crystal. For example, in a cubic lattice, (111) looks the same as (1 $\bar{1}$ 1) after rotation (and possibly reflection) of the axes of the crystal (but would never look like (122) under any rotation or reflection since the spacing between planes is different!).¹⁵ If we want to describe all lattice planes that are equivalent in this way, we write {111} instead.

It is interesting that lattice planes in crystals were well understood long before people even knew for sure there was such a thing as atoms. By studying how crystals cleave along certain planes, scientists like Miller and Bravais could reconstruct a great deal about how these materials must be assembled.¹⁶

13.2 Brillouin Zones

The whole point of going into such gross detail about the structure of reciprocal space is in order to describe waves in solids. In particular, it will be important to understand the structure of the Brillouin zone.

13.2.1 Review of One-Dimensional Dispersions and Brillouin Zones

As we learned in Chapters 9–11, the Brillouin zone is extremely important in describing the excitation spectrum of waves in periodic media. As a reminder, in Fig. 13.4 we show the excitation spectrum of vibrations of a diatomic chain (Chapter 10) in both the reduced, and extended zone schemes. Since waves are physically equivalent under shifts of the wavevector k by a reciprocal lattice vector $2\pi/a$, we can always express every excitation within the first Brillouin zone, as shown in the reduced zone scheme (top of Fig. 13.4). In this example, since there are two atoms per unit cell, there are precisely two excitation modes per wavevector. On the other hand, we can always unfold the spectrum and put the lowest (acoustic) excitation mode in the first Brillouin zone and the higher-energy excitation mode (optical) in the second Brillouin zone, as shown in the extended zone scheme (bottom of Fig. 13.4). Note that there is a jump in the excitation spectrum at the Brillouin zone boundary.

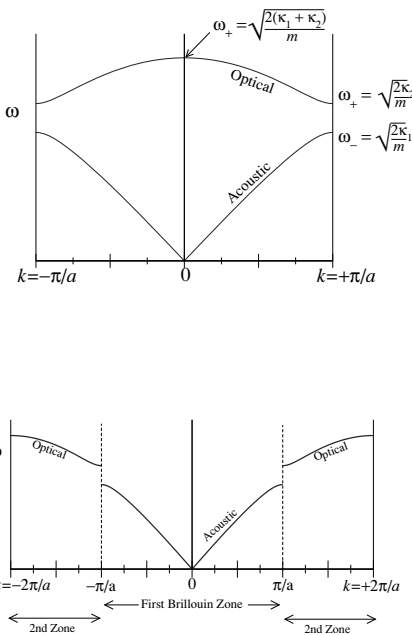


Fig. 13.4 Phonon spectrum of a diatomic chain in one dimension. **Top:** Reduced zone scheme. **Bottom:** Extended zone scheme. (See Figs. 10.6 and 10.8.) We can display the dispersion in either form due to the fact that wavevector is only defined modulo $2\pi/a$, that is, it is periodic in the Brillouin zone.

13.2.2 General Brillouin Zone Construction

Definition 13.4 A *Brillouin zone* is any primitive unit cell of the reciprocal lattice.

Entirely equivalent to the one-dimensional situation, physical waves in crystals are unchanged if their wavevector is shifted by a reciprocal lattice vector $\mathbf{k} \rightarrow \mathbf{k} + \mathbf{G}$. Alternately, we realize that the physically relevant quantity is the crystal momentum. Thus, the Brillouin zone has been defined to include each physically different crystal momentum exactly once (each \mathbf{k} point within the Brillouin zone is physically different, and all physically different points occur once within the zone).

While the most general definition of Brillouin zone allows us to choose any shape primitive unit cell for the reciprocal lattice, there are some definitions of unit cells which are more convenient than others.

We define the *first Brillouin zone* in reciprocal space quite analogously to the construction of the Wigner–Seitz cell for the direct lattice.

Definition 13.5 Start with the reciprocal lattice point $\mathbf{G} = \mathbf{0}$. All \mathbf{k} points which are closer to $\mathbf{0}$ than to any other reciprocal lattice point define the **first Brillouin zone**. Similarly all \mathbf{k} points where the point $\mathbf{0}$ is the second closest reciprocal lattice point to that point constitute the **second Brillouin zone**, and so forth. Zone boundaries are defined in terms of this definition of Brillouin zones.

As with the Wigner–Seitz cell, there is a simple algorithm to construct the Brillouin zones. Draw the perpendicular bisector between the point $\mathbf{0}$ and each of the reciprocal lattice vectors. These bisectors form the Brillouin zone boundaries. Any point that you can get to from $\mathbf{0}$ without crossing a perpendicular bisector is in the first Brillouin zone. If you cross only one perpendicular bisector, you are in the second Brillouin zone, and so forth.

In Fig. 13.5, we show the Brillouin zones of the square lattice. A few general principles to note:

- (1) The first Brillouin zone is necessarily connected, but the higher Brillouin zones typically are made of disconnected pieces.
- (2) A point on a Brillouin zone boundary lies on the perpendicular bisector between the point $\mathbf{0}$ and some reciprocal lattice point \mathbf{G} . Adding the vector $-\mathbf{G}$ to this point necessarily results in a point (the same distance from $\mathbf{0}$) which is on another Brillouin zone boundary (on the bisector of the segment from $\mathbf{0}$ to $-\mathbf{G}$). This means that Brillouin zone boundaries occur in parallel pairs symmetric around the point $\mathbf{0}$ which are separated by a reciprocal lattice vector (see Fig. 13.5).
- (3) Each Brillouin zone has exactly the same total area (or volume in three dimensions). This must be the case since there is a one-to-one mapping of points in each Brillouin zone to the first Brillouin zone. Finally, as in one dimension, we claim that there are exactly as many k -states within the first Brillouin zone as there are unit cells in the entire system.¹⁷

Note, that as in the case of the Wigner–Seitz cell construction, the shape of the first Brillouin zone can look a bit strange, even for a relatively simple lattice (see Fig. 12.7).

The construction of the Brillouin zone is similar in three dimensions as it is in two, and is again entirely analogous to the construction of the Wigner–Seitz cell in three dimensions. For a simple cubic lattice, the first Brillouin zone is simply a cube. For fcc and bcc lattices, however, the situation is more complicated. As we mentioned in the **Aside** at the end of Section 13.1.3, the reciprocal lattice of the fcc lattice is bcc,

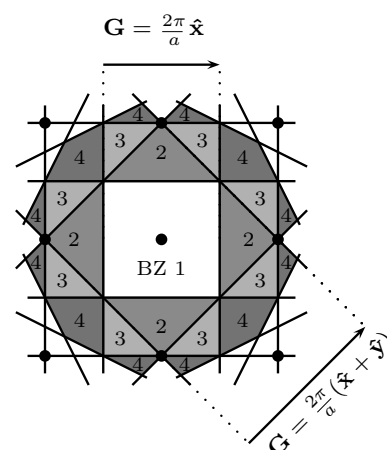


Fig. 13.5 First, second, third, and fourth Brillouin zones of the square lattice. All of the lines drawn in this figure are perpendicular bisectors between the central point $\mathbf{0}$ and some other reciprocal lattice point. Note that zone boundaries occur in parallel pairs symmetric around the central point $\mathbf{0}$ and are separated by a reciprocal lattice vector.

¹⁷Here's the proof for a square lattice. Let the system be N_x by N_y unit cells. With periodic boundary conditions, the value of k_x is quantized in units of $2\pi/L_x = 2\pi/(N_x a)$ and the value of k_y is quantized in units of $2\pi/L_y = 2\pi/(N_y a)$. The size of the Brillouin zone is $2\pi/a$ in each direction, so there are precisely $N_x N_y$ different values of \mathbf{k} in the Brillouin zone.

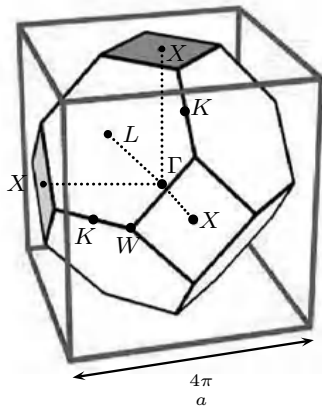


Fig. 13.6 First Brillouin zone of the fcc lattice. Note that it is the same shape as the Wigner–Seitz cell of the bcc lattice, see Fig. 12.13. Special points of the Brillouin zone are labeled with code letters such as X , K , and Γ . Note that the lattice constant of the conventional unit cell is $4\pi/a$ (see Exercise 13.1).

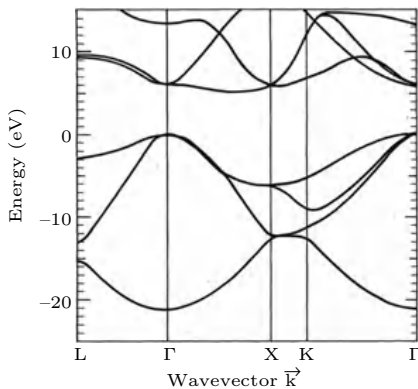


Fig. 13.7 Electronic excitation spectrum of diamond ($E = 0$ is the Fermi energy). The momentum, along the horizontal axis is taken in straight line cuts between special labeled points in the Brillouin zone. Figure is from J. R. Chelikowsky and S. G. Louie, *Phys. Rev. B* **29**, 3470 (1984), <http://prb.aps.org/abstract/PRB/v29/i6/p3470-1>. Copyright American Physical Society. Used by permission.

and vice-versa. Thus, the Brillouin zone of the fcc lattice is the same shape as the Wigner–Seitz cell of the bcc lattice! The Brillouin zone for the fcc lattice is shown in Fig. 13.6 (compare to Fig. 12.13). Note that in Fig. 13.6, various k -points are labeled with letters. There is a complicated labeling convention that we will not discuss, but it is worth knowing that it exists. For example, we can see in the figure that the point $\mathbf{k} = \mathbf{0}$ is labeled Γ , and the point $\mathbf{k} = (2\pi/a)\hat{y}$ is labeled X .

Now that we can describe the fcc Brillouin zone, we finally have a way to properly describe the physics of waves in some real crystals!

13.3 Electronic and Vibrational Waves in Crystals in Three Dimensions

In Fig. 13.7 we show the electronic band-structure (i.e., dispersion relation) of diamond, which can be described as an fcc lattice with a diatomic basis (see Fig. 12.21). As in the one-dimensional case, we can work in the reduced zone scheme where we only need to consider the first Brillouin zone. Since we are trying to display a three-dimensional spectrum (energy as a function of \mathbf{k}) on a one-dimensional diagram, we show several single-line cuts through reciprocal space.¹⁸ Starting on the left of the diagram, we start at the L -point of the Brillouin zone and show $E(\mathbf{k})$ as \mathbf{k} traces a straight line to the Γ point, the center of the Brillouin zone (see Fig. 13.6 for the labeling of points in the zone). Then we continue to the right and \mathbf{k} traces a straight line from the Γ point to the X point. Then we make a straight line from X to K and then X back to Γ .¹⁹ Note that the lowest band is quadratic at the center of the Brillouin zone (a dispersion $\hbar^2 k^2 / (2m^*)$ for some effective mass m^*).

Similarly, in Fig. 13.8, we show the phonon spectrum of diamond. There are several things to note about this figure. First of all, since diamond has a unit cell with two atoms in it (it is fcc with a basis of two atoms) there should be six modes of oscillation per k -points (three directions of motion times two atoms per unit cell). Indeed, this is what we see in the picture, at least in the central third of the picture. In the other two parts of the picture, one sees fewer modes per k -point, but this is because, due to the symmetry of the crystal along this particular direction, several excitation modes have exactly the same energy. (Note examples at the X -point where two modes come in from the right, but only one goes out to the left. This means the two modes have the same energy on the left of the X point.) Secondly, we note that at the Γ -point, $\mathbf{k} = \mathbf{0}$, there are exactly three modes which come down linearly to zero energy. These are the three acoustic modes—the higher one being a longitudinal mode and the lower two being transverse. The other three modes, which are finite energy at $\mathbf{k} = \mathbf{0}$, are the optical modes.

¹⁸This type of plot, because it can look like a jumble of lines, is sometimes called a “spaghetti diagram”.

¹⁹In fact if one travels in a straight line from X to K and continues in a straight line, one ends up at Γ in the neighboring Brillouin zone!

Chapter Summary

- The reciprocal lattice is a lattice in k -space defined by the set of points such that $e^{i\mathbf{G}\cdot\mathbf{R}} = 1$ for all \mathbf{R} in the direct lattice. Given this definition, the reciprocal lattice can be thought of as the Fourier transform of the direct lattice.
- A reciprocal lattice vector \mathbf{G} defines a set of parallel equally spaced planes via $\mathbf{G}\cdot\mathbf{r} = 2\pi m$ such that every point of the direct lattice is included in one of the planes. The spacing between the planes is $d = 2\pi/|\mathbf{G}|$. If \mathbf{G} is the smallest reciprocal lattice vector parallel to \mathbf{G} then this set of planes is a family of lattice planes, meaning that all planes intersect points of the direct lattice.
- Miller Indices (h, k, l) are used to describe families of lattice planes, or reciprocal lattice vectors.
- The general definition of Brillouin zone is any unit cell in reciprocal space. The first Brillouin zone is the Wigner–Seitz cell around the point $\mathbf{0}$ of the reciprocal lattice. Each Brillouin zone has the same volume and contains one k -state per unit cell of the entire system. Parallel Brillouin zone boundaries are separated by reciprocal lattice vectors.

References

For reciprocal lattice, Miller indices and Brillouin zones, I recommend:

- Ashcroft and Mermin, chapter 5 (Again be warned of the nomenclature issue mentioned in Chapter 12, margin note 1.)
- Dove, chapter 4

Many books introduce X-ray diffraction and the reciprocal lattice at the same time. Once you have read the next chapter and studied scattering, you might go back and look at the nice introductions to reciprocal space given in the following books:

- Goodstein, sections 3.4–3.5 (very brief)
- Kittel, chapter 2
- Ibach and Luth, chapter 3
- Glazer, chapter 4

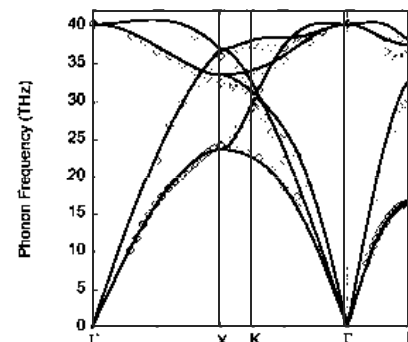


Fig. 13.8 Phonon spectrum of diamond (points are from experiment, solid line is a modern theoretical calculation). Figure is from A. Ward et al., *Phys. Rev. B* **80**, 125203 (2009), <http://prb.aps.org/abstract/PRB/v80/i12/e125203>, Copyright American Physical Society. Used by permission.

Exercises

(13.1) Reciprocal Lattice

Show that the reciprocal lattice of a fcc (face-centered cubic) lattice is a bcc (body-centered cubic) lattice. Correspondingly, show that the reciprocal lattice of a bcc lattice is an fcc lattice. If an fcc lattice has conventional unit cell with lat-

tice constant a , what is the lattice constant for the conventional unit cell of the reciprocal bcc lattice? Consider now an orthorhombic face-centered lattice with conventional lattice constants a_1, a_2, a_3 . What is the reciprocal lattice now?

(13.2) **Lattice Planes**

Consider the crystal shown in Exercise 12.3. Copy this figure and indicate the [210] direction and the (210) family of lattice planes.

(13.3) **Directions and Spacings of Crystal Planes**

▷ † Explain briefly what is meant by the terms “crystal planes” and “Miller indices”.

▷ Show that the general direction $[hkl]$ in a cubic crystal is normal to the planes with Miller indices (hkl) .

▷ Is the same true in general for an orthorhombic crystal?

▷ Show that the spacing d of the (hkl) set of planes in a cubic crystal with lattice parameter a is

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

▷ What is the generalization of this formula for an orthorhombic crystal?

(13.4) † **Reciprocal Lattice**

(a) Define the term Reciprocal Lattice.

(b) Show that if a lattice in 3d has primitive lattice vectors \mathbf{a}_1 , \mathbf{a}_2 and \mathbf{a}_3 then primitive lattice vectors for the reciprocal lattice can be taken as

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \quad (13.13)$$

$$\mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \quad (13.14)$$

$$\mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \quad (13.15)$$

What is the proper formula in 2d?

(c) Define tetragonal and orthorhombic lattices. For an orthorhombic lattice, show that $|\mathbf{b}_j| = 2\pi/|\mathbf{a}_j|$. Hence, show that the length of the reciprocal lattice vector $\mathbf{G} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$ is equal to $2\pi/d$, where d is the spacing of the (hkl) planes (see question 13.3)

(13.5) **More Reciprocal Lattice**

A two-dimensional rectangular crystal has a unit cell with sides $a_1 = 0.468$ nm and $a_2 = 0.342$ nm.

(a) Draw to scale a diagram of the reciprocal lattice.

▷ Label the reciprocal lattice points for indices in the range $0 \leq h \leq 3$ and $0 \leq k \leq 3$.

(b) Draw the first and second Brillouin zones using the Wigner–Seitz construction.

(13.6) **Brillouin Zones**

(a) Consider a cubic lattice with lattice constant a . Describe the first Brillouin zone. Given an arbitrary wavevector \mathbf{k} , write an expression for an equivalent wavevector within the first Brillouin zone (there are several possible expressions you can write).

(b) Consider a triangular lattice in two dimensions (primitive lattice vectors given by Eqs. 12.3). Find the first Brillouin zone. Given an arbitrary wavevector \mathbf{k} (in two dimensions), write an expression for an equivalent wavevector within the first Brillouin zone (again there are several possible expressions you can write).

(13.7) **Number of States in the Brillouin Zone**

A specimen in the form of a cube of side L has a primitive cubic lattice whose mutually orthogonal fundamental translation vectors (primitive lattice vectors) have length a . Show that the number of different allowed \mathbf{k} -states within the first Brillouin zone equals the number of primitive unit cells forming the specimen. (One may assume periodic boundary conditions, although it is worth thinking about whether this still holds for hard-wall boundary conditions as well.)

(13.8) **Calculating Dispersions in $d > 1^*$**

(a) In Exercises 9.8 and 11.9 we discussed dispersion relations of systems in two dimensions (if you have not already solved those exercises, you should do so now).

▷ In Exercise 11.9, describe the Brillouin zone (you may assume perpendicular lattice vectors with length a_1 and a_2). Show that the tight-binding dispersion is periodic in the Brillouin zone. Show that the dispersion curve is always flat crossing a zone boundary.

▷ In Exercise 9.8, describe the Brillouin zone. Show that the phonon dispersion is periodic in the Brillouin zone. Show that the dispersion curve is always flat crossing a zone boundary.

(b) Consider a tight binding model on a three-dimensional fcc lattice where there are hopping matrix elements $-t$ from each site to each of the nearest-neighbor sites. Determine the energy spectrum $E(\mathbf{k})$ of this model. Show that near $\mathbf{k} = \mathbf{0}$ the dispersion is parabolic.