3   What is a crystal structure?

> "In mathematics, if a pattern occurs, we can go on to ask, Why does it occur? What does it signify? And we can find answers to these questions. In fact, for every pattern that appears, a mathematician feels he ought to know why it appears."
>
> W. W. Sawyer, mathematician

3.1 Introduction

In this chapter, we will analyze the various components that make up a *crystal structure*. We will proceed in a rather pragmatic way, and begin with a loose "definition" of a crystal structure that most of us could agree on:

A crystal structure is a regular arrangement of atoms or molecules.

We have some idea of what atoms and molecules are – at least, we think we do . . . And we also have some understanding of the words "regular arrangement." The word "regular" could imply the existence of something that repeats itself, whereas "arrangement" would imply the presence of a *pattern*. But, there are many possible patterns: the words on this page form a pattern of lines; migrating birds often fly in V-shaped formations; musicians in a marching band walk in an orderly way; the kernels on a piece of corn are arranged in neatly parallel rows; and so on. All of these words, *regular arrangement, pattern, orderly, repeats itself,* are commonly used words in our everyday language, but they are not sufficiently precise for a scientific description of what a crystal structure really is.

Fig. 3.1. (a) A periodic pattern consisting of (b) a 2-D net and (c) a motif. The motif is repeated at each point of the 2-D net, to create the pattern in (a).
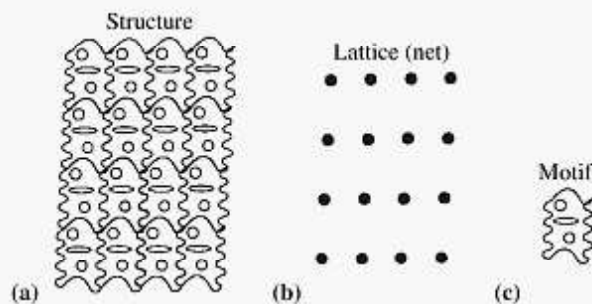
So, we will need to define more rigorously what we mean by a regular arrangement. We can understand this concept intuitively by considering the drawing in Fig. 3.1. Figure 3.1(a) shows a periodic drawing; although this is clearly not a drawing of a crystal structure, the drawing does illustrate some of the more fundamental aspects of crystals. The drawing consists of a *motif*, shown in Fig. 3.1(c), which is repeated by translating it from one point, chosen as the origin in Fig. 3.1(b), to other points arranged in a two-dimensional pattern. The set of points constitutes what we will call a *net* in two dimensions (2-D) and a *lattice* in three dimensions (3-D). The motif represents the *decoration* of that net/lattice. In exactly the same way, a crystal structure can be described as a 3-D lattice, decorated with atoms or molecules. Hence, our "regular arrangement" is now restricted to be a "lattice." In the next section, we will describe in a more rigorous way what a lattice is.

Before we do so, let us return to one of the examples of patterns given in the previous paragraph: the *marching band*. Consider a marching band in which the members occupy positions on 10 rows of 3 musicians each. When the band assembles itself into this formation, the rows and columns are well defined, and all musicians are nicely lined up, with the nearest musicians in front, behind, and to left and right at, say, 1.5 meters from each other. Once the band starts marching, however, it becomes much harder for the musicians to maintain this formation with great accuracy; as a spectator, we expect them to keep their formation as best they can, and, not infrequently, the band which does this best may also end up being more popular (assuming their music sounds good, too!). Depending on the discipline and/or motivation of the band members, the formation may remain nearly perfect throughout the march (as would be expected for a military marching band), or it may be more loosely related to the original formation, with each musician staying within, say, half a meter of his/her supposed position. At any moment in time, only a few of the musicians will be precisely at their nominal position, but on average, over the duration of the march, all of them will have been where they were supposed to be. This is illustrated in Fig. 3.2: (a) shows the initial positions on a regular square grid. At an instant of time, each musician may deviate somewhat from these positions. In (b), the trajectory of each musician during

Fig. 3.2. (a) Initial positions of the musicians of a marching band (atoms on a crystal lattice); (b) trajectories of all musicians relative to their initial position for the length of the march for a loosely structured band (atoms at elevated temperature), and (c) for a highly disciplined band (atoms at low temperature).
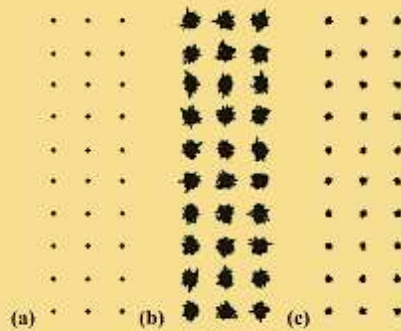
the entire march is drawn with respect to that musician's initial position. It is clear that, on average, the musicians did keep to the initial formation. The size of the "trajectory cloud" around each site is an indication of how much each musician deviated on average from the formation. For a military marching band, we would expect the diameter of these clouds to be very small, as shown in (c).

Now we can abandon the marching band and replace each band member by an atom.[1] The atoms are positioned on a grid and, as a function of time, they move around their own grid site in a somewhat random way. The surrounding atoms prevent them from moving too far from their initial positions, so that, on average, over a relatively long time, each atom appears to occupy the perfect grid position. The magnitude of the instantaneous deviations is determined, not by motivation or discipline, but by the *temperature* of the atom assembly. A high temperature means that the atoms have a high kinetic energy, so their excursions from the average position can become quite large; whereas at a low temperature, there is insufficient kinetic energy available for large excursions, and the *vibration amplitude* will remain small. This kind of atom motion is known as *thermal motion* or *thermal vibration*. It is present in every crystal structure and it is convenient to ignore it in a structural description of crystals.[2] The thermal motion of atoms only becomes important in the determination of the crystal structure by means of a suitable form of radiation (X-rays, electrons, neutrons) and can be adequately described by means of the so-called *Debye–Waller factor*, which will be introduced in Chapter 11. From here on, we will always consider the average position to be the "real" position of the atom; this is an approximation, but it turns out to be a very convenient

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[1] The reader who also happens to be a member of a marching band may rest assured: there will be no further verbal abuse of marching bands in this book!

[2] Thermal vibration is not limited to materials with a crystalline structure; it also occurs in liquids and gases, where there is no periodic structure. The vibrations are related to the curvature of the interatomic interaction potential introduced in the previous chapter. A small curvature around the equilibrium distance indicates a small restoring force for excursion away from this position; hence, the vibration frequency will be low. For a large curvature, the restoring force is large, and therefore the vibration frequency is high.

one because most mathematical relations to be derived in the remainder of this book become independent of time.

The average position of an atom in a crystal structure does not change with time, so we can slightly revise our initial loose definition of a crystal structure to:

A crystal structure is a time-invariant, three-dimensional arrangement of atoms or molecules on a lattice.

We will take this statement as a starting point for this chapter. First, we need to define more precisely what we mean by the term "lattice."

3.2 The space lattice

3.2.1 Basis vectors and translation vectors

The historical comments in Box 3.1 show how René-Just Haüy built models of crystals by stacking rectangular blocks in such a way that the assembly resembled the external shape (or *form*) of macroscopic crystals. By assuming the existence of a single shape, he was able to construct many different forms, thereby explaining the large variety of crystal forms (or shapes) observed in nature. We will take Haüy's block model as the starting point for the introduction of the space lattice. First of all, we consider the most general block shape, an outline of which is shown in Fig. 3.3. If we take one of the corners of the block as the origin, then we can define three vectors along the three edges of the block. We shall call them **a**, **b**, and **c**. Note that the angles between these vectors need not be 90°, and that the lengths of these vectors need not be the same.
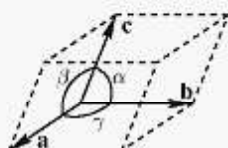
The main advantage of defining these basis vectors is that we can easily identify the coordinates of all of the corners of the block. For instance, the corner opposite the origin has position vector $\mathbf{a} + \mathbf{b} + \mathbf{c}$. Alternatively, we can write the *coordinates* of this point as $(1, 1, 1)$, since the position vector corresponds to $1 \times \mathbf{a} + 1 \times \mathbf{b} + 1 \times \mathbf{c}$. Note that we will always write coordinates between parentheses, with commas separating the individual components.

Next, we consider a stack of blocks, as in Haüy's models. Since each block is identical to every other block, and they are stacked edge to edge and face to face, it is easy to see that we can jump from the origin to *any* corner of any block in the stack, by taking *integer linear combinations* of the three basis vectors. The coordinates of each block corner can therefore be written as triplets of integers, which we will denote by (u, v, w). Note that these integers can take on all possible values, including negative ones, since we can take the origin at any point in the stack.

Fig. 3.3. Illustration of a general building block (a unit cell), with the three basis vectors **a**, **b**, and **c** (figure reproduced from Fig. 1.1 in *Introduction to Conventional Transmission Electron Microscopy,* M. De Graef, 2003, Cambridge University Press).

Box 3.1 Haüy's crystal models

René-Just Haüy (1743–1822) was a French priest and mineralogist. His building block theory of crystal structures led directly to the lattice model (Haüy, 1784, 1801, 1822). He suggested that crystals are composed of arrays of subdivisible blocks, called *integral molecules*, with shapes specific to the crystal. Haüy showed how, replicating the same blocks in different ways, he could construct different external shapes. This was taken as an explanation as to why the same substance could have crystals with different external forms. Haüy showed further that the building block theory implied that the overall symmetry of a crystal must be the same as that of its constituent parts. Nowadays, we no longer talk about "integral molecules," but, instead, we use the name "unit cell." The figure below, taken from Vol. 5 of Haüy (1801), shows how the rhombic dodecahedron shape (on the left) can be obtained by starting from a cubic crystal shape (on the right), and adding layers of cubic building blocks, with each new layer one unit cell smaller on all sides than the previous one.
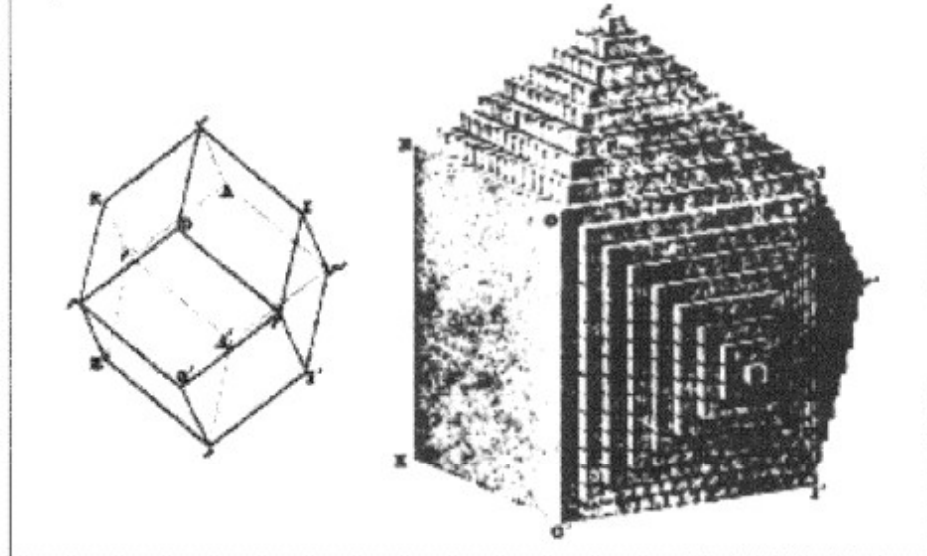
Instead of considering blocks, we will forget about the outline of the blocks, and only consider the corner points. We can then jump from the origin to the point with coordinates (u, v, w) by using the *translation vector* (or *lattice vector*) $\mathbf{t}$, defined as

$$\mathbf{t} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}. \qquad (3.1)$$

All corner points can be reached by integer linear combinations of the three basis vectors. We shall call the collection of corner points the *space lattice*, and each individual corner a *node* or *lattice point*. A space lattice is thus a set of nodes, related to one another by the *translation vectors* $\mathbf{t}$. In 2-D, there

are only two basis vectors, **a** and **b**, and the integer linear combinations of these vectors make up the nodes of the net.

> A space lattice (net) is the geometrical image of the operation of the translation operators on the node at the origin.

3.2.2 Some remarks about notation

At this point, it is useful to introduce a shorthand notation for the translation vector **t**. In addition to writing its components as the integer triplet (u, v, w), we will also write them as (u_1, u_2, u_3), or as u_i $(i = 1 \ldots 3)$. Similarly, we will often write $\mathbf{a}_i$ for the basis vectors, where $\mathbf{a}_1 \equiv \mathbf{a}$, $\mathbf{a}_2 \equiv \mathbf{b}$, and $\mathbf{a}_3 \equiv \mathbf{c}$. This appears to be a superfluous complication of the notation, but it will turn out to be extremely useful for all kinds of crystallographic computations, as we will see in the following chapters.

The *set* (or collection) of translation vectors of any space lattice necessarily contains an infinite number of elements; we will denote this set by the calligraphic symbol $\mathcal{T}$:

$$\mathcal{T} = \{\mathbf{t} \mid \mathbf{t} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}, (u, v, w) \text{ integers}\}. \tag{3.2}$$

This expression reads as follows: $\mathcal{T}$ is the set of all vectors **t** that can be written as linear combinations of the type $u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$, with u, v, and w restricted to be integers.

Before we continue with a description of space lattices, it is worthwhile taking a brief "notational excursion." In crystallographic computations, it is often useful to be as economic as possible with symbols: the fewer symbols needed to describe a concept, the less likely that errors will be made. So, at this point we will introduce a device which will allow us to shorten all the expressions that we have discussed so far. This device is commonly known as the *Einstein summation convention*, and it is stated as follows:

> A summation is implied over every subscript which appears twice on the same side of an equation.

Here is how it works. We start from the expression for the translation vector, and rewrite it in a few different ways, using various notations that we are already familiar with:

$$\begin{aligned}
\mathbf{t} &= u\mathbf{a} + v\mathbf{b} + w\mathbf{c}; \\
&= u_1\mathbf{a}_1 + u_2\mathbf{a}_2 + u_3\mathbf{a}_3; \\
&= \sum_{i=1}^{3} u_i\mathbf{a}_i.
\end{aligned}$$

This last expression uses the summation sign $\sum$. It is obvious that this last expression is shorter in length than the other two, but now it has grown in the vertical direction... We all know that we are living and working in a three-dimensional (3-D) space, so it is rather clear that the sum goes from $i = 1$ to $i = 3$. So, why don't we simply drop the summation sign altogether and write:

$$\boxed{\mathbf{t} \equiv u_i \mathbf{a}_i,}$$ (3.3)

and we remind ourselves that there is an *implied summation* over the index i. We know that there is a summation, *since the index i appears twice on the same side of the equation*, once on the u_i and once on the $\mathbf{a}_i$. This notation convention (dropping the summation signs) is the Einstein summation convention, which we will use profusely throughout this text.[3] Since this looks a little confusing, let's practice this convention on a few examples.

First of all, consider the expression

$$\mathbf{t} = u_j \mathbf{a}_j.$$

Is there an implied summation? Yes, there is, since the subscript j is repeated twice on the same side of the equation! So, this equation really reads as:

$$\mathbf{t} = \sum_{j=1}^{3} u_j \mathbf{a}_j.$$

This also illustrates an important point: it does not matter which letter of the alphabet we use for the subscript, as long as we use the same letter twice. The subscript is therefore known as a *dummy* subscript or a dummy index.

Let's look at a slightly more complicated expression:

$$??? = b_j u_i \mathbf{a}_i.$$

First we deal with the right hand side. The index i occurs twice, so there is a summation implied over i. The index j occurs only once, so there is no summation over j. So, the equation really reads as:

$$??? = b_j \sum_{i=1}^{3} u_i \mathbf{a}_i.$$

But what would we have on the left hand side? That's a good question! If we use the relation $\mathbf{t} = u_i \mathbf{a}_i$, then we would have

$$b_j \mathbf{t} = b_j u_i \mathbf{a}_i.$$

---

[3] The reader may find a comment on the notation used in this book in Box 3.2.

Box 3.2 Alternative notation

There exists an alternative notation, frequently used in the physics literature. This notation employs both subscripts and superscripts. The components of a vector are denoted with superscripts, as in:

$$\mathbf{t} = u^i \mathbf{a}_i = \sum_{i=1}^{3} u^i \mathbf{a}_i.$$

The Einstein summation convention then reads: *A summation is implied over every index which appears twice on the same side of an equation, once as a subscript and once as a superscript.* While there are some advantages of this notation over the one used in this book, in particular when we start describing *reciprocal space* in Chapter 6, the authors decided to simplify the notation, and to only consider subscripts for both vector components and basis vectors.

This illustrates another important rule when working with subscripts: *subscripts must be balanced on both sides of the equation.* This means that, if a subscript is present on one side of the equation, and no summation is implied over this subscript, then it must also be present on the other side of the equation.

Finally, let's look at a more complicated example, which we will encounter in a later chapter:

$$F = \epsilon_{ijk} p_i q_j r_k.$$

Leaving aside for now the exact meaning of the symbol ϵ_{ijk}, simply note that it is possible for symbols to have more than one subscript.[4] We see that there are three different subscripts, and each of them occurs twice, so there must be three summations:

$$F = \sum_{i=1}^{3} \sum_{j=1}^{3} \sum_{k=1}^{3} \epsilon_{ijk} p_i q_j r_k.$$

Since all indices are used up in the summations, there can be no index on the left-hand side of the equation. This concludes some simple examples. We will make extensive use of the summation convention in this text, so it is

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[4] Think about matrices! A 3×3 matrix A has three rows and three columns, and each entry of the matrix is labeled by two subscripts, as in A_{ij}. This stands for the entry on row i and column j. The symbol ϵ_{ijk} is actually a $3 \times 3 \times 3$ matrix, so we need three indices to describe each of its entries.

important for the reader to be familiar with this notation. There are a few more exercises at the end of this chapter.

3.2.3 More about lattices

Having defined what a lattice is, we can take a closer look at the consequences of this definition. If we translate the lattice by any of the lattice vectors **t**, then we obtain the same lattice again. In other words, if you were to look at an infinite lattice, then look away while someone else translates this lattice by **t**, then you would not be able to see the difference between the lattices before and after translation; they would coincide. If the translation vector was not a lattice vector, then you *would* be able to see the difference, since the translated lattice would not coincide with the original one. This means that the lattice is *invariant* under any translation by a lattice vector **t**. As a consequence of this invariance, *all lattice points are identical.* This is illustrated in Fig. 3.4: we can choose any lattice point as the origin, and the surroundings of all lattice points are identical, as indicated by the thin lines around points 0, 1, and 2.

The space lattice is a purely mathematical abstraction and *does not contain any atoms or molecules at all.* However, we can take a molecule and attach it to each lattice point to obtain a crystal structure. We thus find that

> A crystal structure consists of a 3-D space lattice which is decorated with one or more atoms.

The lattice is a 3-D assembly of mathematical points, which reflect the *translational symmetry* of the complete crystal. In general, any 3-D lattice can be fully described by stating the lengths of the 3 basis vectors and their mutual angles. According to the *International Tables for Crystallography* (Hahn, 1989) the following notation should be used to describe the dimensions of a 3-D lattice:

$$
\begin{aligned}
a &= \text{length of } \mathbf{a}; \\
b &= \text{length of } \mathbf{b}; \\
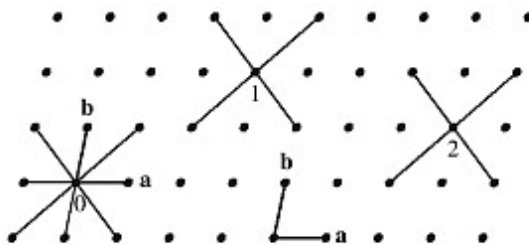c &= \text{length of } \mathbf{c};
\end{aligned}
\tag{3.4}
$$

Fig. 3.4. All lattice points have identical surroundings and every point can be selected as the origin of the lattice.

$$\alpha = \text{angle between } \mathbf{b} \text{ and } \mathbf{c};$$
$$\beta = \text{angle between } \mathbf{a} \text{ and } \mathbf{c};$$
$$\gamma = \text{angle between } \mathbf{a} \text{ and } \mathbf{b}.$$

(3.5)

It is easy to remember the angle designations: for any pair of vectors, say, **a** and **c**, take the missing letter (in this case *b*) and turn it into a greek letter (in this case β). These six quantities fully specify the space lattice (see Fig. 3.3). The choice of the shortest lattice vector as either **a**, **b**, or **c** will depend on the symmetry of the lattice. We will often write the six numbers as $\{a, b, c, \alpha, \beta, \gamma\}$; they are known as the *lattice parameters*. For a 2-D net, the *net parameters* are usually written as $\{a, b, \gamma\}$.

The volume defined by the three basis vectors (shown by the dotted lines in Fig. 3.3) is known as the *unit cell* of the space lattice. It is customary to define the vectors in such a way that the reference frame is right-handed. If the mixed vector product $(\mathbf{a} \times \mathbf{b}) \cdot \mathbf{c}$ is positive, then the reference frame is right-handed; if the product is negative, then the reference frame is left-handed. We will define the dot and cross products in the following chapters. Next, we will attempt to answer the question: *how many different space lattices/nets are there?* We will consider 2-D nets before describing the 3-D lattices.

3.3 The four 2-D crystal systems

Consider the net parameters $\{a, b, \gamma\}$. If we take arbitrary values for all three parameters, then we end up with a net similar to that shown in Fig. 3.5. This is known as an *oblique net*. There are no special conditions on any of the net parameters. The oblique net has a low symmetry;[5] if we place a line normal to the drawing in Fig. 3.5(a), through one of the nodes of the net, then it is easy to see that, if we rotate the net by 180° around this line, all the nodes of the rotated net will coincide with the original nodes. A node at a position $u\mathbf{a} + v\mathbf{b}$ will end up at position $-u\mathbf{a} - v\mathbf{b}$ after the rotation, and this is again an integer linear combination of the basis vectors. This means that the new rotated node coincides with one of the original nodes, so that the original and rotated nets are indistinguishable.

There is one special value for the angle γ. When $\gamma = 90°$, the unit cell of the net becomes a rectangle, and the resulting net is the *rectangular*

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[5] We will define and discuss the concept of symmetry extensively in Chapter 8. For now it is sufficient for the reader to understand what a rotation is.
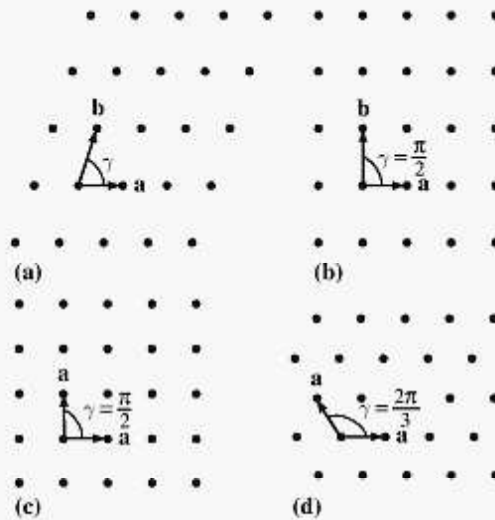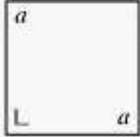
net, illustrated in Fig. 3.5(b). The rectangular net has the same rotational symmetry (a 180° rotation axis normal to the plane of the drawing). In addition, it also has mirror symmetry. This is easily verified by holding this book in front of a mirror and looking at Fig. 3.5(b); there is no difference between the original and its mirror image. For the oblique net, we see that the image in the mirror leans over to the left, whereas the original leans over towards the right. Therefore, the oblique net does not have mirror symmetry, and we say that the rectangular net has a higher symmetry than the oblique net. The net parameters of the rectangular net are usually written as $\{a, b, \pi/2\}$.

Next, we again start from the oblique net, but this time we take the two basis vectors to have equal length, so that the net parameters are $\{a, a, \gamma\}$. In this case, there are two special angles γ, for which the resulting net has a higher symmetry than the oblique net. If $\gamma = 90°$, then the net is based on a square unit cell, and is called the *square net*, as shown in Fig. 3.5(c). The higher symmetry is easy to spot, since a rotation of 90° around any axis going through a node (perpendicular to the plane of the drawing) leaves the net invariant.

Finally, the last 2-D net is obtained by setting $\gamma = 120°$. This is the *hexagonal net*; it is easy to see that this net is invariant under a rotation of 60°, hence the name *hexag*onal. Note that we could also have selected $\gamma = 60°$; the resulting net would have been indistinguishable from the one shown in Fig. 3.5(d). The international convention is to select $\gamma = 120°$ for the hexagonal net. These four nets are the only possible nets that can be generated with only two basis vectors **a** and **b**. We say that, in 2-D, there are only four possible *crystal systems*: *oblique*, *rectangular*, *hexagonal*, and *square*. Table 3.1 summarizes the net parameter symbols, the crystal system name and an example of a unit cell for each of the 2-D crystal systems.

Table 3.1. The four 2-D crystal systems.

Condition/symbol	Crystal system	Drawing
no condition, $\{a, b, \gamma\}$	**OBLIQUE**	
$\gamma = 90°$, $\{a, b, 90°\}$	**RECTANGULAR**	
$a = b, \gamma = 120°$, $\{a, a, 120°\}$	**HEXAGONAL**	
$a = b, \gamma = 90°$, $\{a, a, 90°\}$	**SQUARE**	

3.4 The seven 3-D crystal systems

There are seven fundamentally different combinations of basis vectors in 3-D. In the most general case, we select arbitrary numbers for the set of six lattice parameters $\{a, b, c, \alpha, \beta, \gamma\}$. This generates the *triclinic* or *anorthic* lattice.[6] Figure 3.3 shows an example of a triclinic unit cell. When we translate this unit cell by integer linear combinations of its basis vectors, we obtain the triclinic lattice. No matter how we rotate this lattice, there are no rotation axes for which the lattice is invariant.

Next, we can assign special values to some or all of the lattice parameters, as we did for the 2-D case. We look for combinations of lattice parameters for which we can identify rotational symmetry in the resulting lattice. It turns out that we can have a single 180° rotation axis when two of the

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[6] The name *triclinic* can be split into two parts: *tri* which stands for "three," and *clinic*, which comes from the Greek word *klinein* for "to bend or slope." In other words, we need three angles to describe this unit cell. The second name, *anorthic*, is a combination of *an*, which means "not," and *ortho*, which stands for "perpendicular," meaning that none of the three angles is a right angle.

three angles α, β, and γ are equal to 90°.[7] It is customary to select β to be the angle that is not equal to 90°, so that we arrive at the lattice parameters $\{a, b, c, \pi/2, \beta, \pi/2\}$. This is known as the *monoclinic* lattice.[8] Table 3.2 shows the lattice parameters and conditions for each of the 3-D crystal systems, along with simple sketches of the corresponding unit cells.

If we select two of the lattice parameters, a and b, to be equal to each other then we can create another 3-D lattice by putting the angles equal to 90°, 90°, 120°, or $\{a, a, c, \pi/2, \pi/2, 2\pi/3\}$. This is similar to the hexagonal 2-D net $\{a, a, 2\pi/3\}$, but now there is a third dimension to the unit cell, perpendicular to the 2-D drawing of Fig. 3.5(d). This is known as the 3-D *hexagonal* lattice. Similar to its 2-D analogue, the 3-D hexagonal lattice has a 60° rotation axis along the **c** direction.

If all three lengths a, b, and c are equal to each other, then we find that there is in general no new lattice unless the three angles are also equal to each other: $\{a, a, a, \alpha, \alpha, \alpha\}$. The resulting lattice is known as the *rhombohedral* lattice. Along the direction corresponding to the body diagonal of this unit cell, a rotation of 120° leaves the lattice invariant. An alternative name for this system is *trigonal*, indicating that the three angles are equal to each other.[9]

A special case of the rhombohedral lattice is found when the angle α is set equal to 90°. In that case, $\{a, a, a, \pi/2, \pi/2, \pi/2\}$, we have a *cubic* lattice. Note that there are now several rotation axes that will leave the unit cell invariant. We can rotate the cube by 90° around any axis normal through one of the faces and going through the center of the cube, by 120° around the body diagonals, and by 180° around any axis going through the centers of two edges of opposite sides of the cube. It is also clear that, when we look at a cube in a mirror, we will see the same cube, so that the cube also has mirror symmetry. We will describe all these symmetry properties in a much more systematic way later on in this book. For now, it suffices that the reader obtain just a simple intuitive understanding of what symmetry means.

Starting from the monoclinic unit cell, we can put the angle β equal to 90°, so that we obtain a lattice for which all three angles are equal, but the lengths of the basis vectors are not equal: $\{a, b, c, \pi/2, \pi/2, \pi/2\}$. This is the *orthorhombic* lattice, with a unit cell which is shaped like a right-angled rhombus. This shape will be familiar to the reader, since most packaging boxes have this shape. It is easy to convince yourself that this shape has three 180° rotation axes, going through the centers of opposite faces.
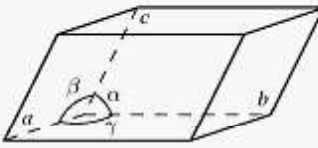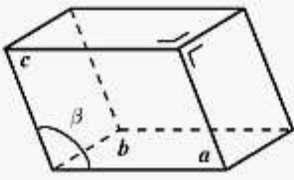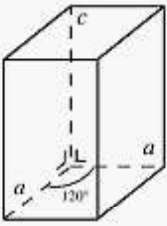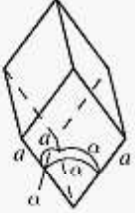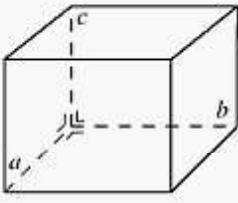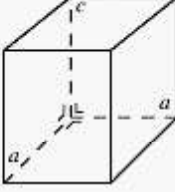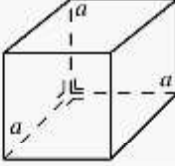
Finally, we can put two of the three parameters of the orthorhombic lattice equal to each other, as in $\{a, a, c, \pi/2, \pi/2, \pi/2\}$. This is the *tetragonal*

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[7] We postpone a more rigorous proof of the existence of the seven 3-D crystal systems until Chapter 8, where we will define all symmetry operators.

[8] *Mono* means "one," indicating that one of the three angles is not a right-angle.

[9] The Greek word *gonia* means "angle."

Table 3.2. The 7 three-dimensional crystal systems.

Condition/symbol	Crystal system	Drawing
no conditions $\{a, b, c, \alpha, \beta, \gamma\}$	**TRICLINIC (ANORTHIC)**	
$\alpha = \gamma = 90°^{\dagger}$ $\{a, b, c, 90, \beta, 90\}$	**MONOCLINIC**	
$a = b,$ $\alpha = \beta = 90°,$ $\gamma = 120°$ $\{a, a, c, 90, 90, 120\}$	**HEXAGONAL**	
$a = b = c,$ $\alpha = \beta = \gamma$ $\{a, a, a, \alpha, \alpha, \alpha\}$	**RHOMBOHEDRAL (TRIGONAL)**	
$\alpha = \beta = \gamma = 90°$ $\{a, b, c, 90, 90, 90\}$	**ORTHORHOMBIC**	
$a = b,$ $\alpha = \beta = \gamma = 90°$ $\{a, a, c, 90, 90, 90\}$	**TETRAGONAL**	
$a = b = c,$ $\alpha = \beta = \gamma = 90°$ $\{a, a, a, 90, 90, 90\}$	**CUBIC**	

† The angle β is usually chosen to be larger than 90°

Fig. 3.6. The seven crystal systems ranked according to symmetry. The closer the system is to the top of the drawing, the higher its symmetry.

Cubic

Hexagonal

Tetragonal

Trigonal

Orthorhombic

Monoclinic

Triclinic
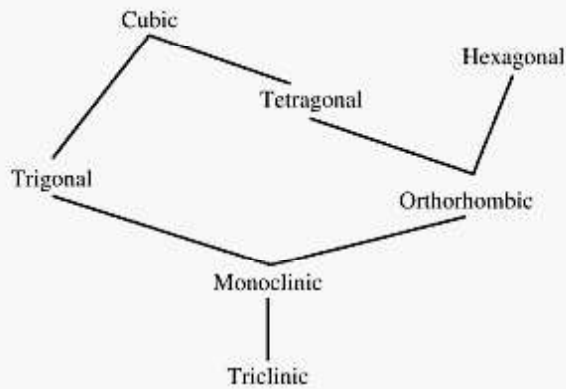
lattice, which has a single rotation axis of 90° going through the centers of the opposite square faces, and 180° rotation angles through the center of the opposite non-square faces. This concludes the enumeration of the seven 3-D crystal systems (Table 3.2).

The 3-D crystal systems can be ranked by their symmetry (for a more complete description of symmetry, see Chapter 8). This ranking is shown in Fig. 3.6. Starting from the cubic symmetry, we can, by successive distortions, create a triclinic lattice.

3.5 The five 2-D Bravais nets and fourteen 3-D Bravais lattices

Consider the 2-D lattice in Fig. 3.7. We can define a unit cell for this lattice in an infinite number of ways; a few possibilities are shown in the figure. The unit cells numbered 1, 2, and 3 are so-called *primitive* unit cells, because they contain only one lattice point. The number of nodes in a cell can be computed in two different ways:

(i) Displace the outline of the unit cell, so that the corners of the cell no longer coincide with lattice sites. Now count the number of sites inside the displaced unit cell. This is illustrated by the dashed cell outlines in Fig. 3.7.
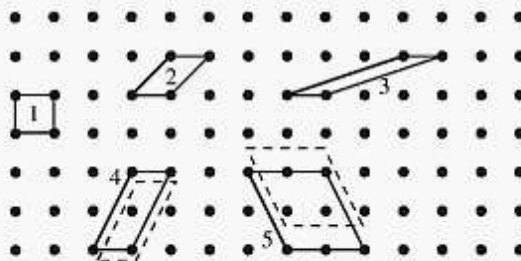
Fig. 3.7. A few possible unit cells in a 2-D square net.

(ii) In 2-D, count the number of sites inside the unit cell (N_{in}); add to that 1/2 of the number of sites on the unit cell boundaries (N_{edge}), and add to that 1/4 of the sites on the unit cell corners (N_{corner}). In other words:

$$N_{2D} = N_{in} + \frac{1}{2}N_{edge} + \frac{1}{4}N_{corner}.$$

In 3-D, the total number of sites in a unit cell is given by:

$$N_{3D} = N_{in} + \frac{1}{2}N_{face} + \frac{1}{4}N_{edge} + \frac{1}{8}N_{corner},$$

where N_{face} is the number of sites in the faces of the unit cell.

For all three of the cells 1, 2, and 3, we find that there are 4 sites located at the corners and none inside or on the edges, hence the number of sites in the unit cell is 1.

The unit cells numbered 4 and 5 in Fig. 3.7 are *non-primitive* unit cells, because they contain more than one lattice site. From the displaced unit cell outlines (indicated with a dashed line) we find that there are $N_{2D} = 2$ for cell 4, and $N_{2D} = 4$ for cell 5. Although these cells could be used to describe this 2-D net, they are not as convenient as cell 1. In general, one describes a lattice with the simplest (not necessarily the smallest) possible unit cell, in this case cell 1. Note also that cell 1 is the only cell of the five shown that reflects the squareness of the net. It is useful to select as unit cell, the cell that reflects the *symmetry* of the net. This is also true for 3-D lattices.

From the definitions of the seven 3-D crystal systems, we know that there are seven primitive unit cells. They are denoted by a two-letter symbol: the first letter (lowercase) indicates the crystal system (*a* for anorthic or triclinic, *m* for monoclinic, *o* for orthorhombic, *t* for tetragonal, *h* for hexagonal, *c* for cubic, and, strangely enough, *no letter* for trigonal or rhombohedral). The second letter (uppercase) indicates the type of cell, which in this case is *primitive* or *P*. The exception to this rule is the rhombohedral or trigonal system, which is indicated by the symbol *R*. The primitive cubic unit cell is hence represented by the symbol *cP*, the primitive tetragonal cell by *tP*, etc.

We can then ask: can we add additional lattice points to the primitive lattices or nets, in such a way that we still have a lattice (net) belonging to the same crystal system? We will first illustrate this for the 2-D nets. We know that, in order for a collection of nodes to form a net, the surroundings of each node must be identical. If we consider a rectangular net with lattice parameters $\{a, b, \pi/2\}$, and add a node at the position $\mathbf{a}/3 + \mathbf{b}/2$, as shown in Fig. 3.8(a), then it is clear that the surroundings of the point A are not the same as those of the point B. While A has as a neighbor the point located at $\mathbf{r}_B = \mathbf{a}/3 - \mathbf{b}/2$ from A, this point B does not have a point located at $\mathbf{a}/3 - \mathbf{b}/2$ from itself (this location is indicated by a gray circle). Therefore, the surroundings of A and B are not identical, so this is not a net. There

Fig. 3.8. (a) Adding the point $r_B = a/3 + b/2$ to each unit cell of a rectangular net does not produce a new net, since all points are no longer identical; (b) adding the point $r_B = (a+b)/2$, produces the centered rectangular net. A primitive cell for this net is shown in gray.
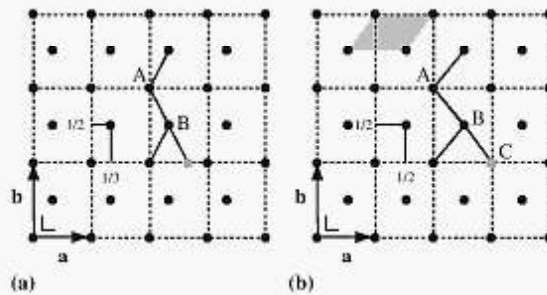
is, however, a special position B inside the rectangular unit cell, for which the surroundings are identical to those of A. This is the point at the center of the cell, as shown in Fig. 3.8(b). If $r_B = (a+b)/2$, then there is a point located at this position relative to B, namely the point C. Hence, the surroundings of A, B, and C are identical – in fact, all of the nodes have identical surroundings – so that this is a new net.

The attentive reader might say: "*Wait a minute! This is not a new net, because I can select a smaller, primitive unit cell (in gray in Fig. 3.8(b)) which fully defines this net. Furthermore, this primitive cell indicates that this net is an oblique net, not a rectangular one!*" This is absolutely correct. We could indeed use the primitive cell to describe the complete net. However, this primitive oblique cell does not reveal that the net actually has a higher symmetry! Indeed, looking at the primitive unit cell in a mirror, we see that the mirror image is not the same as the original cell. The mirror image of the rectangular cell with a node at its center *is* the same as the original, so it makes sense to use this non-primitive cell to describe the net. This simple example illustrates two important ideas:

- It is always possible to define a primitive unit cell, for every possible net (this is also true for 3-D lattices).
- If a non-primitive cell can be found, that describes the symmetry of the net (lattice), then that cell should be used to describe the net (lattice). Since the surroundings of every node must be identical, we can only add new nodes at locations that are *centered* in the middle between the original lattice sites.

The 2-D net shown in Fig. 3.8(b) is, therefore, a new net, known as the *centered rectangular net*. If we try to do the same thing with the other 2-D nets, we find (this is left as an exercise for the reader) that there are no new nets to be found. We conclude that in 2-D, there are only five possible nets: four of them are primitive (oblique, rectangular, hexagonal, and square) and one is centered (centered rectangular). We call these five nets the *2-D Bravais nets*. The five 2-D Bravais nets are shown in Fig 3.9.

We can repeat this procedure in three dimensions. In this case, there are three possible ways to add nodes at the center in between existing nodes.

Fig. 3.9. The five
two-dimensional Bravais
lattices.
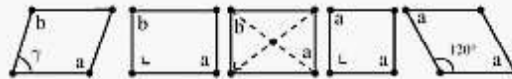
- *Body centering*: we add a lattice site in the center of the unit cell, at the location $(1/2, 1/2, 1/2)$. For every site $\mathbf{t}$, there is then an additional site $\mathbf{t} + (\mathbf{a} + \mathbf{b} + \mathbf{c})/2$. The vector $\mathbf{I} \equiv (\mathbf{a} + \mathbf{b} + \mathbf{c})/2$ is known as the *body centering vector*. Note that this vector is *not* a translation vector of the lattice since its components are not integer numbers. The symbol for a body centered lattice is I, from the German word for body centered: "Innenzentriert."

- *Face centering*: we add a lattice site to the center of all faces of the unit cell, at the locations $(1/2, 1/2, 0)$, $(1/2, 0, 1/2)$, and $(0, 1/2, 1/2)$. For every site $\mathbf{t}$ there are then three additional sites $\mathbf{t} + (\mathbf{a} + \mathbf{b})/2$, $\mathbf{t} + (\mathbf{a} + \mathbf{c})/2$, and $\mathbf{t} + (\mathbf{b} + \mathbf{c})/2$. The vectors $\mathbf{C} = (\mathbf{a} + \mathbf{b})/2$, $\mathbf{B} = (\mathbf{a} + \mathbf{c})/2$, and $\mathbf{A} = (\mathbf{b} + \mathbf{c})/2$ are known as the *face centering vectors*. The symbol for a face centered lattice is F.

- *Base centering*: we add a lattice site to the center of only one face of the unit cell, at the location $(1/2, 1/2, 0)$ *or* $(1/2, 0, 1/2)$ *or* $(0, 1/2, 1/2)$. The base centering vectors are identical to the face centering vectors, except that only one of them is present. If the plane formed by the basis vectors $\mathbf{a}$ and $\mathbf{b}$ is centered, then the lattice is known as a C-centered lattice. If the $\mathbf{a}$–$\mathbf{c}$ plane is centered, the lattice is B-centered and if the $\mathbf{b}$–$\mathbf{c}$ plane is centered then the lattice is A-centered.

One can show that for two-face centering not all lattice points have the same surroundings, and hence two-face centering cannot give rise to a new lattice.

We can now apply these five forms of centering (A, B, C, I, and F) to all seven primitive unit cells. In several cases we do generate a new lattice, in other cases we can redefine the unit cell and reduce the cell to another type. Consider the following example. The primitive tetragonal unit cell *tP* shown in Figure 3.10(a) is C-centered in Fig. 3.10(b). This is not a new cell, however, since we can redefine the unit cell by the thick lines in Fig. 3.10(c), which form a new, smaller *primitive tetragonal* unit cell with lattice parameter $a_1 = a\sqrt{2}/2$. We find that a C-centered tetragonal cell *tC* is equivalent to tP and hence does not form a new lattice. Repeating this exercise for all possible
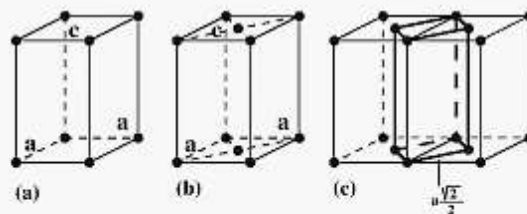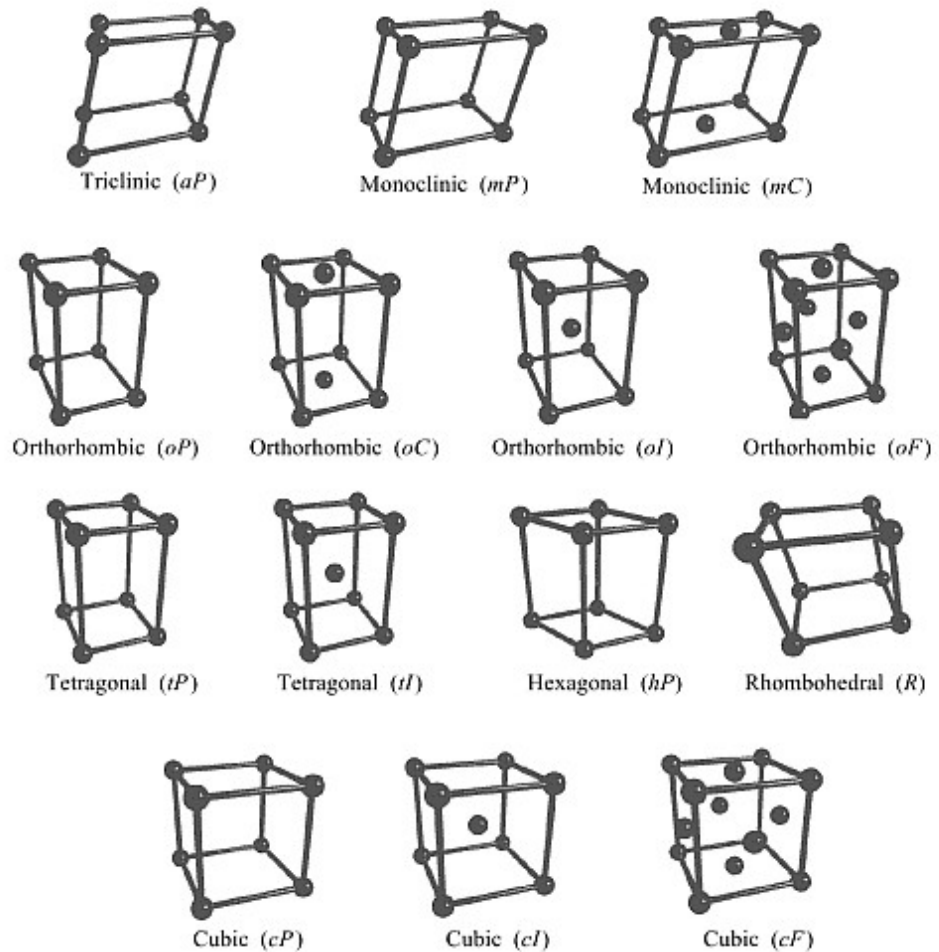

Fig. 3.10. (a) *tP* lattice, (b) *tC*
lattice, (c) equivalence of *tC*
and *tP* lattices.

Fig. 3.11. The fourteen 3-D Bravais lattices.

Triclinic (aP)   Monoclinic (mP)   Monoclinic (mC)

Orthorhombic (oP)   Orthorhombic (oC)   Orthorhombic (oI)   Orthorhombic (oF)

Tetragonal (tP)   Tetragonal (tI)   Hexagonal (hP)   Rhombohedral (R)

Cubic (cP)   Cubic (cI)   Cubic (cF)

types of lattice centering (there are $5 \times 7 = 35$ possibilities!) we end up with seven additional lattice types that cannot be reduced to primitive ones of the same crystal system: mC, oC, oI, oF, tI, cI, and cF. All fourteen 3-D Bravais lattices are shown in Fig. 3.11.

3.6 Other ways to define a unit cell

It is always possible to describe a lattice with a primitive unit cell. Hence, all 14 Bravais lattices can be described by primitive cells, even when they are centered. As an example, consider the cF lattice in Fig. 3.12a. By selecting shorter vectors $\mathbf{a}_p$, $\mathbf{b}_p$, and $\mathbf{c}_p$ we can define a primitive rhombohedral unit cell with angle $\alpha = 60°$. This cell does not reflect the cubic symmetry of the cF lattice, but is has the advantage that it contains only one lattice site. In solid state physics, it is often convenient to work with the primitive unit cells of all the Bravais lattices, rather than with their non-primitive (and higher symmetry) versions.
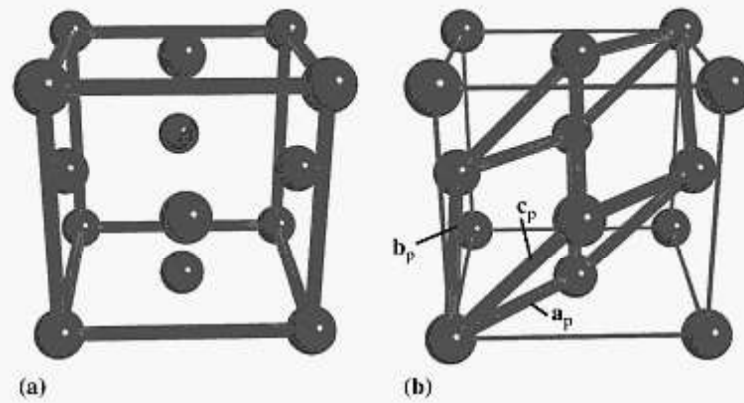
(a)   (b)
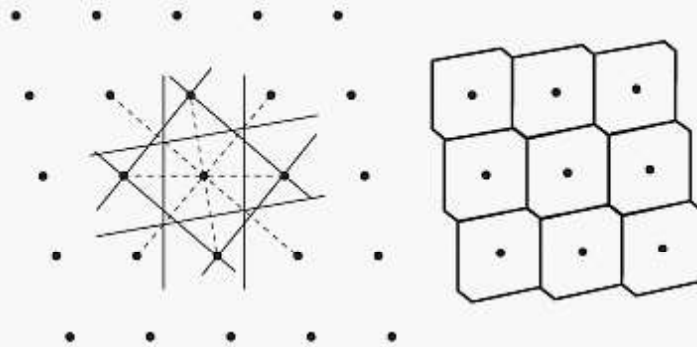
There is yet another useful way to define a unit cell: the *Wigner–Seitz cell*. The Wigner–Seitz (WS) cell corresponding to a particular lattice point is *the region of space which is closer to that particular lattice point than to any other lattice point*. It is straightforward to construct the WS cell (see Fig. 3.13): construct the vector between the origin and one of the neighboring lattice points. Draw the perpendicular plane through the midpoint of this vector. This plane separates space into two regions, each of which contains all of the points closer to one of the endpoints of the vector than to the other endpoint. Repeat this construction for all other lattice points. The smallest volume around the selected point enclosed by all these planes is the Wigner–Seitz cell. Note that the WS cell can have more than six sides in 3-D, or more than 4 in 2-D. All WS cells are primitive by construction and they do display the true symmetry of the underlying lattice. In 3-D, it can be shown that there are 24 topologically different Wigner–Seitz cells for the 14 Bravais lattices (Burns and Glazer, 1990). These cells have different shapes, depending on the actual values of the lattice parameters. An example of the WS cell for the cI Bravais lattice is shown in Fig. 3.14. The WS cell is also known as the *Voronoi domain*, the *Dirichlet domain*, or the *domain of influence* of a given lattice point. It can be shown on theoretical grounds that the number of faces of a 3-D WS cell is always between 6 and 14 (inclusive). In 2-D, the number of edges of the WS cell lies between 4 and 6. Inspection of Fig. 3.14 reveals that the WS cell has the

Fig. 3.14. The Wigner–Seitz cell (b) for the body centered cubic Bravais lattice (a). This shape has fourteen faces, six of them are squares, the other eight are hexagons.

(a)   (b)
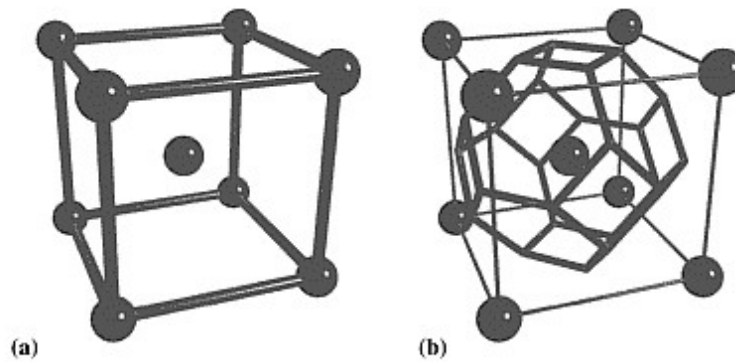
same symmetry as the Bravais lattice. This is true for the general WS cell as well.

In spite of the possibly complicated shape of the Wigner–Seitz cell, it is often very easy to compute its volume. The difficult way would be to actually use geometry to determine the volume. However, there is a much easier method. We know that the *cI* Bravais lattice is a cubic lattice, so that the volume of the unit cell is a^3, where a is the edge length. We also know that there are 2 nodes in the unit cell (the one in the center counts as a whole, whereas the 8 at the corners count for 1/8 each). So, the volume per node is equal to $a^3/2$. If we take the WS cell for this Bravais lattice, then two of those WS cells must still be equal to the volume a^3; the shape is different, but the available volume must be the same. Therefore, in spite of its complicated shape, the volume of the WS cell for the *cI* Bravais lattice is simply $a^3/2$.

In summary, there are fourteen Bravais lattices and we can define three types of unit cells to describe them: the conventional unit cell, the primitive unit cell, and the Wigner–Seitz cell. Of these three, only the conventional cell and the Wigner–Seitz cell display the true symmetry of the underlying lattice.

3.7 Historical notes

Moritz Frankenheim (1801–69) was a German crystallographer who was the first to enumerate the 32 crystal classes. He was also the first to enumerate the 14 three-dimensional lattices, but his list contained an error. In 1850, **August Bravais** (1811–63), a French naval officer and scientist, showed that two of Frankenheim's lattices were identical, and he subsequently correctly derived the 14 lattices that now carry his name (Bravais, 1850). After the classification of crystals into seven axial systems, the question of which symmetry operations were compatible with these crystal systems was addressed and first solved correctly by Frankenheim. In 1830, **J. F. C. Hessel** (1796–1872, Fig. 9.15(b) on page 228) independently solved the problem of the symmetries compatible with the seven axial systems, i.e., he found that only 2-, 3-, 4-, and

(a)   (b)
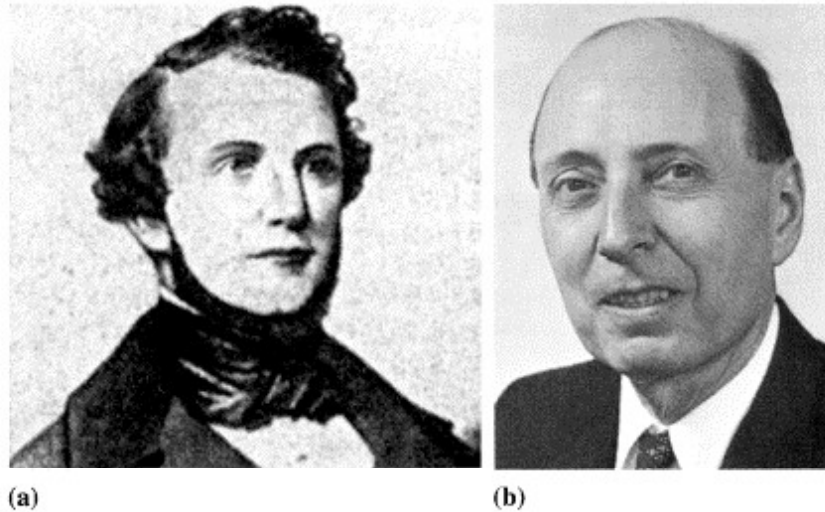
6-fold rotation axes were compatible with the translational lattice symmetry. Neither his work nor the work by Frankenheim were noticed by scientists at the time.

Eugene Paul Wigner (1902–95) was a Hungarian scientist. While at the Technische Hochschule in Berlin, he learned about the role of symmetry in crystallography. At about the same time, the new quantum mechanics was being developed, and Wigner immediately realized the importance of symmetry principles in quantum mechanics. His work in this area earned him the 1963 Nobel prize in physics. After a short stay at the University of Göttingen, he moved to Princeton, where he worked on solid state physics, along with his first graduate student, **Frederick Seitz**. The Wigner–Seitz cell, as introduced in this chapter, results from their joint research. Wigner applied the mathematics of irreducible representations of groups to a variety of physics problems; he became especially well known for his ground-breaking paper on the relativistic Lorentz transformation and for his work on the algebra of angular momentum coupling in quantum mechanics. Wigner's interest in nuclear physics and his knowledge of chemistry were instrumental in his design of a full scale nuclear reactor, which was to become the basis for the commercial Dupont reactors in the post World War II years. In his later years, Wigner founded the quantum theory of chaos.

3.8 Problems

(i) *Bravais lattices I:* Show that a face centered tetragonal lattice (tF) can be reduced to one of the 14 Bravais lattices. Write the basis vectors of this Bravais lattice in terms of those of the tF lattice.

(ii) *Bravais lattices II:* Consider the cubic Bravais lattices *cP*, *cI*, and *cF*, each with lattice parameter a. Make a table showing for each lattice the number of first nearest neighbour lattice sites N_1, the distance to those neighbours d_1, the number of second nearest neighbour lattice sites N_2, and the distance to those neighbours d_2.

(iii) *Bravais lattices III:* Describe the consecutive deformations that need to be applied to a cubic unit cell to turn it into a monoclinic unit cell; repeat the question for the deformation of a tetragonal cell into a triclinic cell.

(iv) *Bravais lattices IV:* Show, using a graphical example, that is not possible to create a new Bravais lattice which has two centered faces (e.g., both A and B centering).

(v) *Other unit cells:* Determine graphically the 3-D primitive unit cell corresponding to the *cI* Bravais lattice and express its lattice parameters in terms of the cubic ones.

(vi) *Wigner–Seitz cells I:* Make a drawing of the Wigner–Seitz unit cell for the *hP* lattice and compute the volume of this cell. (Hint: this does not require any actual computations. The volume can be derived simply by thinking about the definition of the WS cell.)

(vii) *Wigner–Seitz cells II:* Compute the volume of the largest sphere that can be inscribed in the Wigner–Seitz cell of the *cI* lattice. (Hint: As in the previous question, this does not really require any significant computations.)

(viii) *fcc Wigner–Seitz cell:* Construct the Wigner–Seitz cell for the *fcc* lattice.

(ix) *bcc Wigner–Seitz cell:* Show that the fractional coordinates of the vertices of the Wigner–Seitz cell of the *bcc* lattice in the $x = 0$ plane are $(0, 1/2, 1/4)$, $(0, 1/2, 3/4)$, $(0, 1/4, 1/2)$, and $(0, 3/4, 1/2)$.

(x) *fcc molecular solid:* Fullerites (discussed in more detail in Chapter 25) have *Buckminsterfullerene* C_{60} molecules decorating the sites of an *fcc* Bravais lattice. The reported low temperature lattice constant, $a_0 = 1.404(1)$ nm for *fcc* C_{60}.

(a) Calculate the number of C atoms contained in the cubic cell.

(b) Calculate the touching molecular sphere radius of C_{60} in the structure.

(c) What is the coordination number, CN of C_{60} molecules about another in this structure.

(xi) *Cubic lattices packing fractions:* Determine directions in which hard spheres touch, and the volume fractions occupied by them in three cubic structures:

$$sc \quad \frac{\pi}{6}; \qquad bcc \quad \frac{\pi\sqrt{3}}{8}; \qquad fcc \quad \frac{\pi\sqrt{2}}{6}.$$

Fig. 3.16. Monoclinic unit cell.

$$\alpha = \gamma = 90°$$
$$\{a, b, c, 90, \beta, 90\}$$

MONOCLINIC
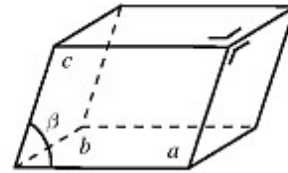
(xii) *Monoclinic crystal system:* Consider the monoclinic unit cell illustrated in Fig. 3.16. Give an example of a 2-fold rotational symmetry and mirror plane that leaves this lattice invariant. (i.e., show an axis about which you can rotate the cell and a plane through which you can reflect the cell and not tell it apart.)