

PART I

STRUCTURE

Picture with me an old cottage nestled in the woods. There is a small house built of clay bricks that were thoughtfully stacked and interlaced by a master brick-layer so as to produce a repeated interlocking pattern. The house has a thatched roof consisting of bundles of straw. The straws in each bundle are oriented in a common direction to direct rainwater off the roof, and are lashed together with twine. Around the house is a garden enclosed by a stone wall. Like the brick walls of the house, the stones in the wall are bonded together with mortar. But unlike the bricks, the stones lack any sense of a repeating pattern.

In this part of the textbook, we examine the basic structures that are found in condensed matter as well as the forces (the mortar and twine) that maintain these structures over long time periods. For our purposes, structures are divided into two main categories: ordered (like the bricks and the straw of the house) and disordered (like the stones in the garden wall).

We begin in Chapter 1 with an examination of the structure of crystals whose periodic arrangement of atoms is a prime example of ordered matter. Particle positions in the crystal are well-defined and the periodic structure is seen to extend for very long distances. As a result of this ordering, crystal structures are rather easy to describe mathematically and provide an excellent introduction to the concept of symmetry. All of this simplicity and symmetry is lost for amorphous materials and in Chapter 2 we examine alternative means for quantifying structures in which particle positions are aperiodic. In the third chapter, we pause to examine the inter-particle forces that provide the mortar necessary for condensed matter to form. There we survey the fundamental types of bonds and discuss how each can influence the resulting structure. In our final chapter on the topic of structures, we look at magnetic materials. Although the atoms that compose these materials may be arranged in an ordered manner, their magnetic moments can either be oriented randomly or, like the aligned straws of a thatched roof, assume an ordered configuration.

Cambridge University Press

978-1-107-01710-8 - Fundamentals of Condensed Matter and Crystalline Physics: An Introduction for Students of Physics and Materials Science

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Excerpt

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1

Crystal structure

Introduction

We often think of crystals as the gemstones we give to a loved one, but most metals (e.g. copper, aluminum, iron) that we encounter daily are common crystals too. In this chapter, we will examine the structure of crystalline matter in which particles are arranged in a repeating pattern that extends over very long distances. This long-range order is formally described by identifying small local groupings of particles, known as a *basis* set, that are identically affixed to the sites of a regularly repeating space *lattice*. As it happens, most crystals found in nature assume one of a limited set of special space lattices known as Bravais lattices. These lattices are special by virtue of their unique symmetry properties wherein only discrete translations and rotations allow the lattice to appear unchanged. Chief among these Bravais lattices are the cubic and hexagonal lattice structures that appear most frequently in nature. We focus extra attention on both to provide a useful introduction to coordination properties and packing fractions.

1.1 Crystal lattice

Crystals have a decided advantage because of the inherent repeating pattern present in their structure. In an ideal (perfect) crystal, this repeating pattern extends indefinitely. However, for real crystals found in nature, the pattern is often interrupted by imperfections known as *defects* that can include vacancies, in which a single particle is missing, and dislocations in which the repeating pattern is offset. These defects are important for some crystal properties, but for now we restrict ourselves to only ideal structures. Besides, even in real crystals large regions containing substantial numbers of particles exist in which a perfectly repeating pattern is maintained.

Let's start with an imaginary, two-dimensional example of a crystal that contains two types of particles (say, large A atoms and small B atoms) as illustrated in Fig. 1.1. It is clear from inspection that this collection of particles displays a well-ordered repeating pattern of A and B atoms that can be

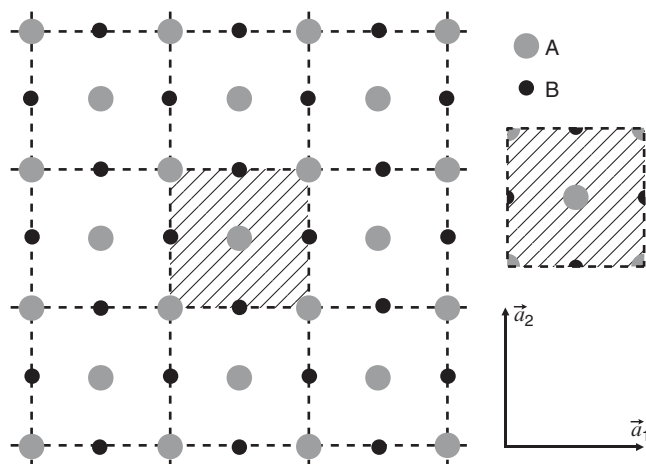


Figure 1.1

The repeating pattern of atoms A (gray circles) and B (black circles) is mapped onto a lattice (dashed lines) that is defined by two lattice vectors (\vec{a}_1 and \vec{a}_2). The pattern of atoms can be viewed as the result of attaching tiles (hashed area that contains a total of two A atoms and two B atoms) onto the lattice.

arranged neatly on the square grid that is superimposed. How can we best describe this repeating pattern? We could simply establish an arbitrary origin and then list the position vectors for every particle of each type. But that would be unnecessarily cumbersome given that there is an obvious repeating pattern. Instead, consider the square grid. The points formed by the intersections of these grid lines can be referenced from any other point by any combination of translations of the form:

$$\vec{T} = h\vec{a}_1 + k\vec{a}_2, \quad (1.1)$$

where h and k are the complete set of integer numbers. The complete set of these translations define what is known as a *space lattice* – an abstract set of points in space that convey the inherent repeating pattern behind the crystal's structure.

In Fig. 1.1, we see that some of the larger A atoms are located directly on the points of the space lattice (grid) and their positions can be referenced by the set of translations in Eq. (1.1) alone. But other A atoms, as well as the smaller B atoms, reside off the lattice. To completely describe the particle positions of all the atoms of the crystal, we must combine with the space lattice a small subset of atoms (known as a *basis*) that are repeatedly attached to each lattice site so as to produce the entire structure. This is much like flooring your kitchen with linoleum tiles. Imagine that each linoleum tile has a pattern stamped onto it corresponding to one of the squares in Fig. 1.1. This particular tile would have two of each type of atom: a complete A atom at the center, one-quarter of an A atom at each corner, and one-half of a B atom at the middle of

each side. When each such tile is positioned with its lower left-hand corner coincident with a space lattice point, the completed assembly of tiles would reproduce the crystal structure of Fig. 1.1 as a whole.

1.1.1 Basis set

Thus, to describe the entire structure of a crystal we combine a space lattice, described by the translations of Eq. (1.1), with a set of basis vectors (referenced to, say, the lower left-hand corner of the tile) to describe the contents of each tile:

$$\vec{R}_i = x_i \vec{a}_1 + y_i \vec{a}_2, \tag{1.2}$$

where x_i and y_i are fractions. For the particular tile illustrated in Fig. 1.1, the basis vectors would include:

$$\begin{aligned} \text{single central A atom: } & \vec{R}_1 = \frac{1}{2} \vec{a}_1 + \frac{1}{2} \vec{a}_2 \\ \text{four corner A atoms: } & \left. \begin{aligned} \vec{R}_2 &= 0 \vec{a}_1 + 0 \vec{a}_2 \\ \vec{R}_3 &= 1 \vec{a}_1 + 0 \vec{a}_2 \\ \vec{R}_4 &= 0 \vec{a}_1 + 1 \vec{a}_2 \\ \vec{R}_5 &= 1 \vec{a}_1 + 1 \vec{a}_2 \end{aligned} \right\} \frac{1}{4} \text{ of an A atom each} \\ \text{four side B atoms: } & \left. \begin{aligned} \vec{R}_6 &= \frac{1}{2} \vec{a}_1 + 0 \vec{a}_2 \\ \vec{R}_7 &= 0 \vec{a}_1 + \frac{1}{2} \vec{a}_2 \\ \vec{R}_8 &= 1 \vec{a}_1 + \frac{1}{2} \vec{a}_2 \\ \vec{R}_9 &= \frac{1}{2} \vec{a}_1 + 1 \vec{a}_2 \end{aligned} \right\} \frac{1}{2} \text{ of a B atom each} \end{aligned}$$

This is still more cumbersome than necessary. Consider, as shown in Fig. 1.2, an alternative space lattice composed of diagonal grid lines. Notice that we

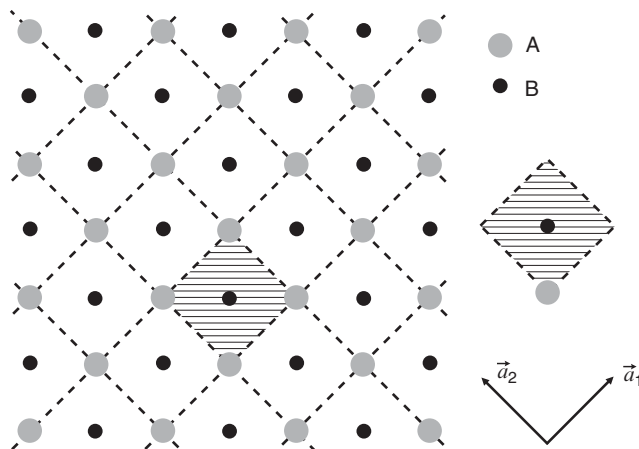


Figure 1.2

The same pattern of two atoms found in Fig. 1.1 are referenced to an alternative, diagonal lattice with a corresponding redefinition of the tile (hashed area) to contain only one each of each atom.

have not repositioned any of the particles, only redefined the space lattice we choose to associate with them. Our diamond-shaped tiles now contain only one atom of each type. This sort of tile is known as a *primitive cell*. It is the smallest-sized tile that can be used together with the space lattice to fill the space with our desired repeating pattern. Our basis set now requires only two vectors:

$$\begin{aligned} \text{A atom: } \vec{R}_1 &= 0\vec{a}_1 + 0\vec{a}_2 \\ \text{B atom: } \vec{R}_2 &= \frac{1}{2}\vec{a}_1 + \frac{1}{2}\vec{a}_2. \end{aligned} \quad (1.3)$$

Note here that the entire A atom is now being associated with the tile (even though three quarters of it sticks outside). Tiles affixed to neighboring lattice sites will then provide the other three A atoms.

1.1.2 Primitive cells

Primitive cells can be identified by several properties. A primitive cell:

- (1) contains only one lattice point,
- (2) has the smallest size (area, $A = |\vec{a}_1 \times \vec{a}_2|$) that can just fill the space by repetition, and
- (3) has a basis set containing only one molecular unit (in our case: AB).

Primitive cells are *not* unique. As shown in Fig. 1.3, yet another alternative space lattice has been chosen to describe our AB system. The shaded cell shown has the same smallest size area as our diamonds in Fig. 1.2 and contains

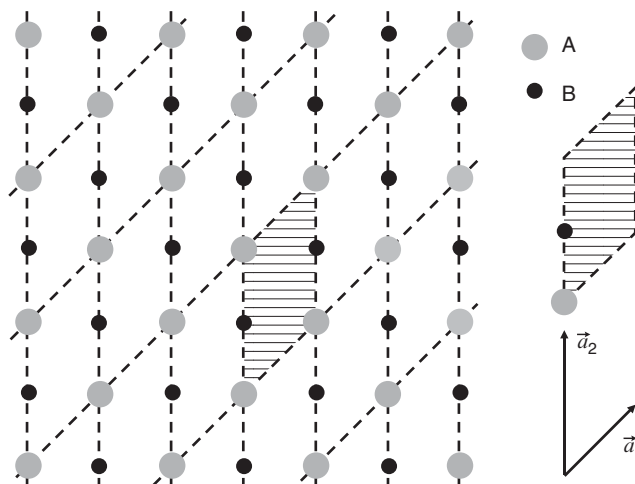


Figure 1.3

The same pattern of two atoms found in Fig. 1.1 and Fig. 1.2 are referenced to yet another alternative lattice with an alternative primitive cell (hashed area).

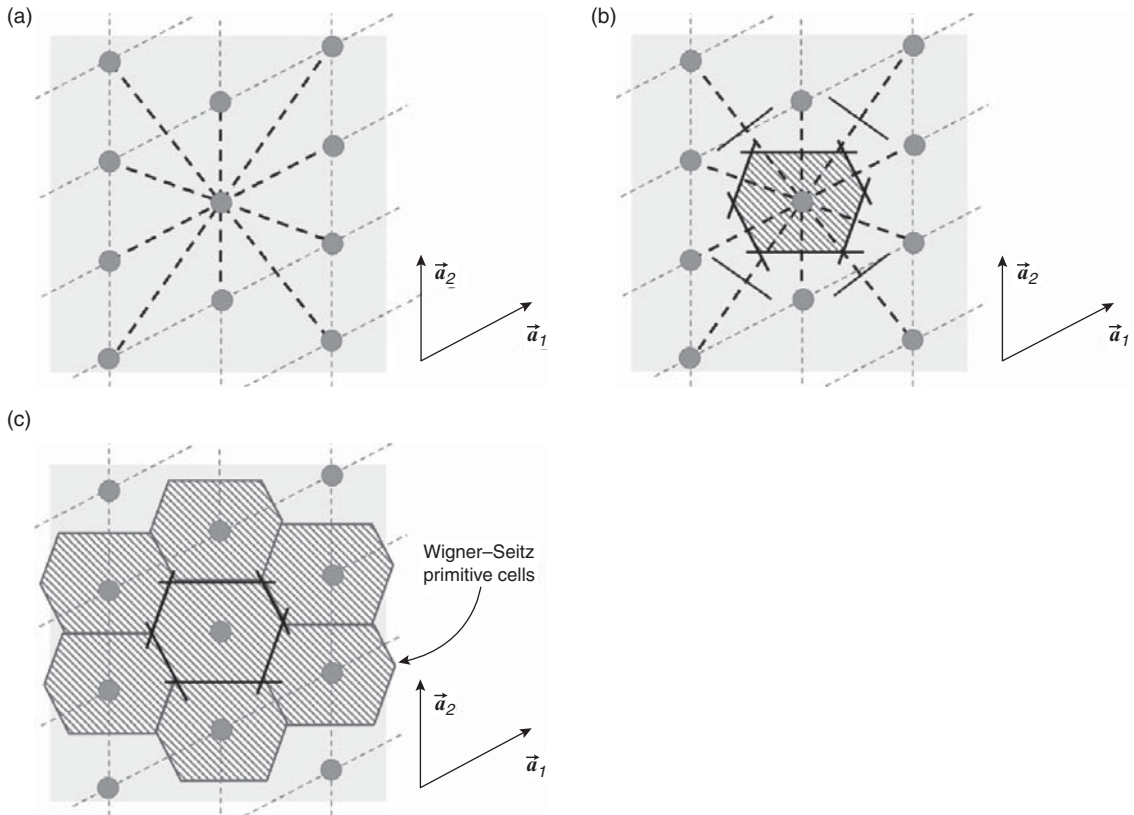


Figure 1.4

Steps in construction of the Wigner–Seitz primitive cell. (a) Lines are first drawn from a central lattice site to all neighboring sites (heavy dashed lines). (b) Each of these lines is then bisected by a perpendicular plane (heavy solid lines) and the volume enclosed becomes the Wigner–Seitz cell. (c) The cell is capable of tiling the entire space and is a primitive cell because it contains one lattice site (at its center).

one of each atom type. However, the basis vectors for this situation would need to be revised as:

$$\begin{aligned} \text{A atom: } \vec{R}_1 &= 0\vec{a}_1 + 0\vec{a}_2 \\ \text{B atom: } \vec{R}_2 &= 0\vec{a}_1 + \frac{1}{2}\vec{a}_2. \end{aligned} \quad (1.4)$$

Wigner–Seitz primitive cell

Although there are many choices for the primitive cell as illustrated above, there is one alternative known as the *Wigner–Seitz cell*, which will have special relevance later on in our discussions of solid state physics. Construction of the Wigner–Seitz cell is illustrated in a series of panels in Fig. 1.4 and begins

by drawing lines from any arbitrary lattice site to neighboring lattice sites (see Fig. 1.4a). Next, each line is bisected by a perpendicular line (or plane in the case of a 3D lattice), as illustrated in Fig. 1.4b. The interior region bounded by these perpendicular lines is then the Wigner–Seitz cell. The cell is seen to be primitive because it contains just one lattice point (namely, the one at its center) and can successfully tile the entire space.

1.2 Symmetry

Aside from its repeating pattern, the space lattice possesses another important characteristic known as *symmetry*. Consider yourself as a (very small) observer located on one of the A atoms in Fig. 1.5. When you look around, you observe nearby B atoms (to the north, south, east and west) and nearby A atoms (to the NE, NW, SE and SW). If you now move to another point of the space lattice (atop another A atom), by a translation, $\vec{T} = h\vec{a}_1 + k\vec{a}_2$, you will experience no sense that your surroundings have changed in any way. In this way the space lattice is said to possess *translational symmetry* – if the entire space lattice is shifted by any of the translation vectors that describe it, the resulting pattern is unchanged in any observable manner.

In addition to this translational symmetry, which all space lattices possess by virtue of their repeating nature, there are other important symmetry operations that define different space lattices. For example, consider yourself again atop an A atom in Fig. 1.5. If you rotate by 90° you again see the same surroundings as before you rotated. The space lattice is said to possess a certain *rotational symmetry*. Note that this symmetry appears only for specific angles of rotation in

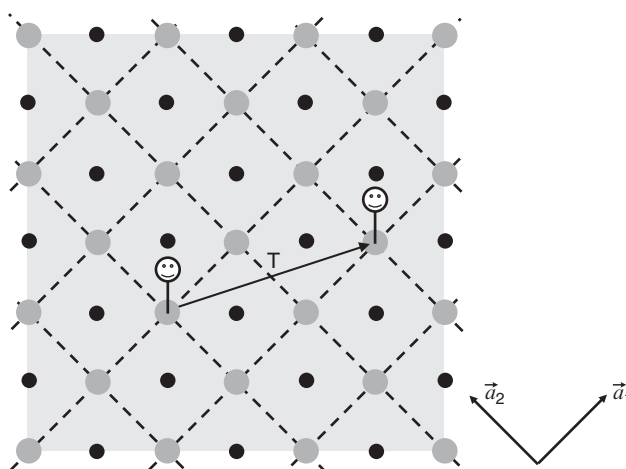


Figure 1.5

An observer situated on a lattice undergoes a translation to any other lattice site and finds his/her surroundings unaltered. The system of particles is then said to possess translational symmetry.

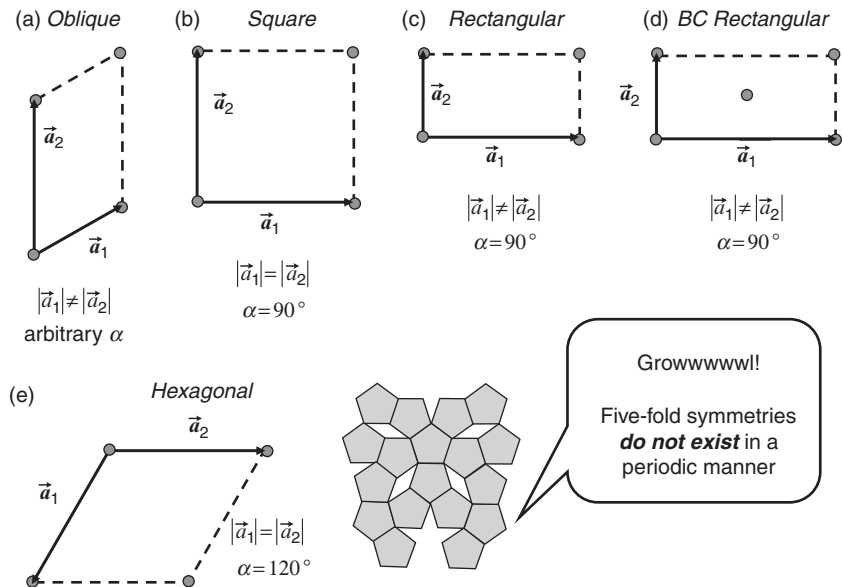


Figure 1.6

The complete set of Bravais lattices (nets) in two dimensions. In addition to the oblique, there are four other lattices possessing distinct symmetry properties. Of these, only the BC rectangular is a conventional lattice. Rotational symmetries include 2, 3 and 4-fold but do not allow for 5-fold symmetries.

the crystal. For example, a rotation by 45° on the lattice of Fig. 1.5 will not return your surroundings to their original state. Only rotations by a multiple of 90° will do this. Because there are four 90° increments in a full circle, this particular case of rotational symmetry is referred to as ‘4-fold’ rotational symmetry.

For the two-dimensional situations we are currently discussing, there are an unlimited number of possible space lattices owing to the fact that any lengths of the two lattice vectors (\vec{a}_1 and \vec{a}_2) can be chosen as well as any angle between them. However, these generic, *oblique* lattices like that shown in Fig. 1.6a will only have 2-fold rotational symmetry unless special restrictions are applied to the lattice vectors. Special lattices, known as *Bravais lattices*, can be obtained with higher degrees of rotational symmetry by placing restrictions on the lengths and angles between the two lattice vectors \vec{a}_1 and \vec{a}_2 . For 2D, there are just four other lattices that can be constructed with other than 2-fold symmetry. These are shown in Fig. 1.6. Note that 5-fold symmetry is not possible. As one can see in Fig. 1.6, primitive cells based on pentagons do not correctly fill space.

Additional symmetry operations under which certain space lattices will return to their original situation include:

- (1) Mirror symmetry: reflection about a plane.
- (2) Inversion symmetry: rotation by 180° about an axis followed by reflection through a plane normal to the rotation axis.

- (3) Glide symmetry: a combination of reflection and translation.
- (4) Screw symmetry: a combination of rotation and translation.

1.2.1 Conventional cells

One of the lattices presented in Fig. 1.6 is not a primitive lattice. The lattice shown in Fig. 1.6d has lattice vectors identical with those in Fig. 1.6c, but has an additional lattice point at the center of the cell. In this instance, the two lattice vectors mark off a *conventional unit cell* (non-primitive) referred to as a ‘body-centered’ (BC) rectangular lattice. Conventional cells are often introduced as an alternative to their primitive lattices as they afford a better visualization of the geometrical structure.

1.3 Bravais lattices

Our discussion of 2D lattices has laid much of the groundwork for discussing lattices in three dimensions. The structures of 3D crystals are again defined by the combination of a space lattice, described by a set of translation vectors:

$$\vec{T} = h\vec{a}_1 + k\vec{a}_2 + l\vec{a}_3, \quad (1.5)$$

where h , k and l are the complete set of integers, and an appropriate set of basis vectors:

$$\vec{R}_i = x_i\vec{a}_1 + y_i\vec{a}_2 + z_i\vec{a}_3, \quad (1.6)$$

that locate the contents of each unit cell in relation to any given lattice point. The volume of a 3D cell is now given by

$$V = |\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3| \quad (1.7)$$

and is smallest for any of the possible primitive cells that can be constructed.

While any sort of generic lattice could be created with appropriate choice of the lengths of the three lattice vectors (\vec{a}_1 , \vec{a}_2 and \vec{a}_3) as well as the angle between them, symmetry considerations lead to only 13 other, special or *Bravais lattices*. All 14 lattice types are illustrated in Fig. 1.7. The generic lattice (with arbitrary lengths and angles between \vec{a}_1 , \vec{a}_2 and \vec{a}_3) is known as the triclinic, and the other 13 are grouped into six sub-categories based on how the lattice vectors are restricted to produce a unique symmetry: monoclinic, orthorhombic, tetragonal, cubic, trigonal and hexagonal. In addition to the primitive cell forms, some of these categories also contain conventional cell forms. These are non-primitive cells in which more than one lattice point is included in the cell. As the majority of crystals found in nature assume either a cubic or a hexagonal lattice structure, we focus next on the detailed properties of these two lattice types.