1
Crystal Structures

Our general objective in this book is to understand the macroscopic properties of solids in a microscopic picture. In view of the many particles in solids, coming up with any microscopic description appears to be a daunting task. It is clearly impossible to solve the equations of motion (classical or quantum mechanical). Fortunately, it turns out that solids are often crystalline, with the atoms arranged on a regular lattice, and this symmetry permits us to solve microscopic models, despite the very many particles involved. This situation is somewhat similar to atomic physics where the key to a description is the spherical symmetry of the atom. We will often imagine a solid as one **single crystal,** a perfect lattice of atoms without any defects whatsoever, and it may seem that such perfect crystals are not particularly relevant for real materials. But this is not the case. Many solids are actually composed of small crystalline grains. These solids are called **polycrystalline,** in contrast to a macroscopic single crystal, but the number of atoms in a perfect crystalline environment is still very large compared to the number of atoms on the **grain boundary**. For instance, for a grain size on the order of 1000^3 atomic distances, only about 0.1% of the atoms are at the grain boundaries. There are, however, some solids that are not crystalline. These are called **amorphous**. The amorphous state is characterized by the absence of any long-range order. There may, however, be some short-range order between the atoms.

This chapter is divided into three parts. In the first part, we define some basic mathematical concepts needed to describe crystals. We keep things simple and mostly use two-dimensional examples to illustrate the ideas. In the second part, we discuss common crystal structures. At this point, we do not ask why the atoms bind together in the way that they do, as this is treated in the next chapter. Finally, we go into a somewhat more detailed discussion of X-ray diffraction, the experimental technique that can be used to determine the microscopic structure of crystals. X-ray diffraction is used not only in solid state physics but also for a wide range of problems in nanotechnology and structural biology.

1.1
General Description of Crystal Structures

Our description of crystals starts with the mathematical definition of the **lattice**. A lattice is a set of regularly spaced points with positions defined as multiples of generating vectors. In two dimensions, a lattice can be defined as all the points that can be reached by the vectors **R**, created from two vectors $\mathbf{a_1}$ and $\mathbf{a_2}$ as

$$\mathbf{R} = m\mathbf{a_1} + n\mathbf{a_2}, \tag{1.1}$$

where n and m are integers. In three dimensions, the definition is

$$\mathbf{R} = m\mathbf{a_1} + n\mathbf{a_2} + o\mathbf{a_3}. \tag{1.2}$$

Such a lattice of points is also called a **Bravais lattice**. The number of possible Bravais lattices that differ by symmetry is limited to 5 in two dimensions and to 14 in three dimensions. An example of a two-dimensional Bravais lattice is given in Figure 1.1. The lengths of the vectors $\mathbf{a_1}$ and $\mathbf{a_2}$ are often called the **lattice constants**.

Having defined the Bravais lattice, we move on to the definition of the **primitive unit cell**. This is any volume of space that, when translated through all the vectors of the Bravais lattice, fills space without overlap and without leaving voids. The primitive unit cell of a lattice contains only one lattice point. It is also possible to define **nonprimitive unit cells** that contain several lattice points. These fill space without leaving voids when translated through a subset of the Bravais lattice vectors. Possible choices of a unit cell for a two-dimensional rectangular Bravais lattice are given in Figure 1.2. From the figure, it is evident that a nonprimitive unit cell has to be translated by a multiple of one (or two) lattice vectors to fill space without voids and overlap. A special choice of the primitive unit cell is the **Wigner–Seitz cell** that is also shown in Figure 1.2. It is the region of space that is closer to one given lattice point than to any other.

The last definition we need in order to describe an actual crystal is that of a **basis**. The basis is what we "put" on the lattice points, that is, the building block for the real crystal. The basis can consist of one or several atoms. It can even consist of
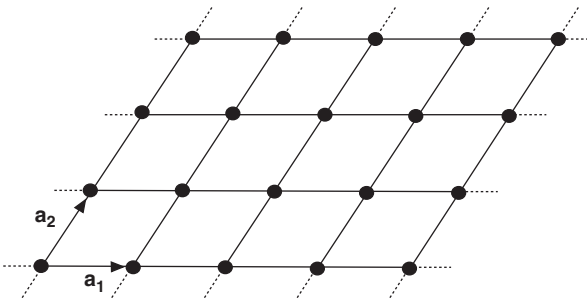

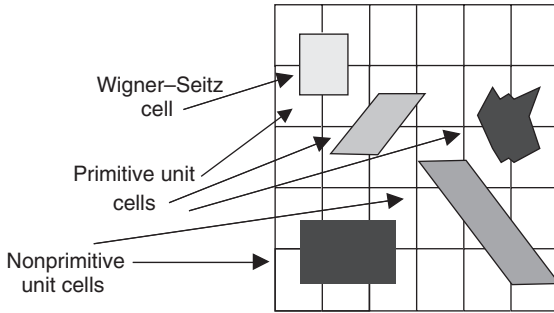**Figure 1.1** Example for a two-dimensional Bravais lattice.

Figure 1.2 Illustration of unit cells (primitive and nonprimitive) and of the Wigner–Seitz cell for a rectangular two-dimensional lattice.

complex molecules as in the case of protein crystals. Different cases are illustrated in Figure 1.3.

Finally, we add a remark about symmetry. So far, we have discussed **translational symmetry**. But for a real crystal, there is also **point symmetry**. Compare the structures in the middle and the bottom of Figure 1.3. The former structure possesses a couple of symmetry elements that the latter does not have, for example, mirror lines, a rotational axis, and inversion symmetry. The knowledge of such symmetries can be very useful for the description of crystal properties.
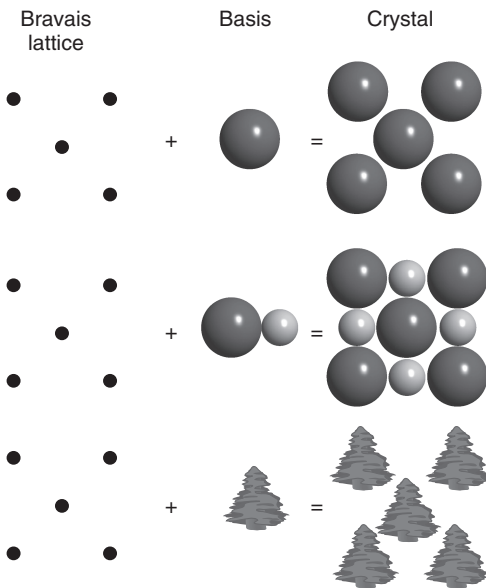

Figure 1.3 A two-dimensional Bravais lattice with different choices for the basis.

1.2
Some Important Crystal Structures

After this rather formal treatment, we look at a number of common crystal structures for different types of solids, such as metals, ionic solids, or covalently bonded solids. In the next chapter, we will take a closer look at the details of these bonding types.

1.2.1
Cubic Structures

We start with one of the simplest possible crystal structures, the **simple cubic structure** shown in Figure 1.4a. This structure is not very common among elemental solids, but it is an important starting point for many other structures. The reason why it is not common is its openness, that is, that there are many voids if we think of the ions as spheres touching each other. In metals, the most common elemental solids, directional bonding is not important and a close packing of the ions is usually favored. For covalent solids, directional bonding *is* important but six bonds on the same atom in an octahedral configuration are not common in elemental solids.

The packing density of the cubic structure is improved in the **body-centered cubic** (bcc) and **face-centered cubic** (fcc) structures that are also shown in Figure 1.4. In fact, the fcc structure has the highest possible packing density for spheres as we shall see later. These two structures are very common. Seventeen elements crystallize in the bcc structure and 24 elements in the fcc structure. Note that only for the simple cubic structure, the cube is identical with the Bravais lattice. For the bcc and fcc lattices, the cube is also a unit cell, but not the primitive one. Both structures are Bravais lattices with a basis containing one atom but the vectors spanning these Bravais lattices are not the edges of the cube.
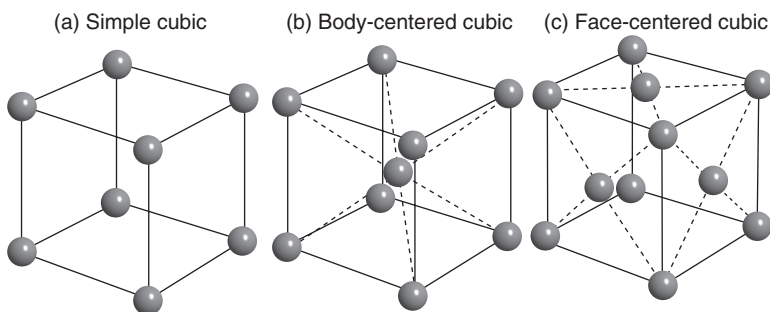
(a) Simple cubic   (b) Body-centered cubic   (c) Face-centered cubic

Figure 1.4 (a) Simple cubic structure; (b) body-centered cubic structure; and (c) face-centered cubic structure. Note that the spheres are depicted much smaller than in the situation of most dense packing and not all of the spheres on the faces of the cube are shown in (c).
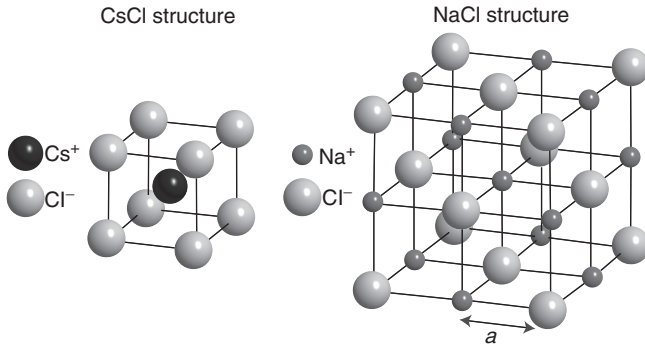
CsCl structure   NaCl structure

Cs⁺

Cl⁻

Na⁺

Cl⁻

a

Figure 1.5 Structures of CsCl and NaCl. The spheres are depicted much smaller than in the situation of most dense packing, but the relative size of the different ions in each structure is correct.

Cubic structures with a more complex basis than a single atom are also important. Figure 1.5 shows the structures of the ionic crystals CsCl and NaCl that are both cubic with a basis containing two atoms. For CsCl, the structure can be thought of as two simple cubic structures stacked into each other. For NaCl, it consists of two fcc lattices stacked into each other. Which structure is preferred for such ionic crystals depends on the relative size of the ions.

1.2.2
Close-Packed Structures

Many metals prefer structural arrangements where the atoms are packed as closely as possible. In two dimensions, the closest possible packing of ions (i.e., spheres) is the hexagonal structure shown on the left-hand side of Figure 1.6. For building a three-dimensional close-packed structure, one adds a second layer as in the middle of Figure 1.6. For adding a third layer, there are then two possibilities. One can either put the ions in the "holes" just on top of the first layer ions, or one can put them into the other type of "holes." In this way, two different crystal structures can be built. The first has an ABABAB... stacking sequence, and the second has an ABCABCABC... stacking sequence. Both have exactly the
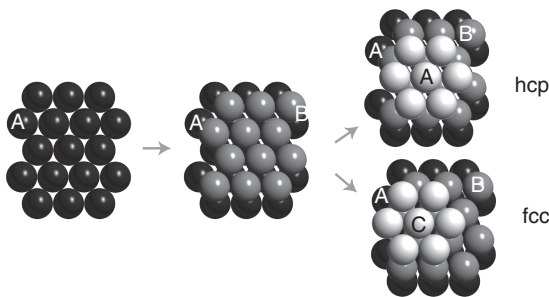
hcp

fcc

Figure 1.6 Close packing of spheres leading to the hcp and fcc structures.

same packing density, and the spheres fill 74% of the total volume. The former structure is called the **hexagonal close-packed structure** (hcp), and the latter turns out to be the fcc structure we already know. An alternative sketch of the hcp structure is shown in Figure 1.14b. The fcc and hcp structures are very common for elemental metals. Thirty-six elements crystallize as hcp and 24 elements as fcc. These structures also maximize the number of nearest neighbors for a given atom, the so-called **coordination number**. For both the fcc and the hcp lattice, the coordination number is 12.

An open question is why, if coordination is so important, not all metals crystallize in the fcc or hcp structure. A prediction of the actual structure for a given element is not possible with simple arguments. However, we can collect some factors that play a role. Not optimally packed structures, such as the bcc structure, have a lower coordination number, but they bring the second-nearest neighbors much closer to a given ion than in the close-packed structures. Another important consideration is that the bonding is not quite so simple, especially for **transition metals**. In these, bonding is not only achieved through the delocalized s and p valence electrons as in **simple metals**, but also by the more localized d electrons. Bonding through the latter has a much more directional character, so that not only the close packing of the ions is important.

The structures of many ionic solids can also be viewed as "close-packed" in some sense. One can arrive at these structures by treating the ions as hard spheres that have to be packed as closely to each other as possible.

1.2.3
Structures of Covalently Bonded Solids

In covalent structures, the atoms' valence electrons are not completely delocalized but shared between neighboring atoms and the bond length and direction are far more important than the packing density. Prominent examples are graphene, graphite, and diamond as displayed in Figure 1.7. Graphene is a single sheet of carbon atoms in a honeycomb lattice structure. It is a truly two-dimensional solid with a number of remarkable properties; so remarkable, in fact, that their
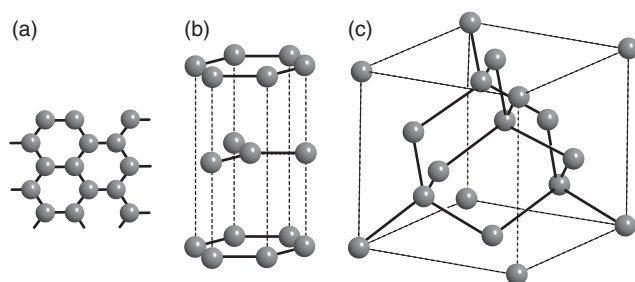

Figure 1.7 Structures for (a) graphene, (b) graphite, and (c) diamond. sp^2 and sp^3 bonds are displayed as solid lines.

discovery has lead to the 2010 Nobel prize in physics being awarded to A. Geim and K. Novoselov. The carbon atoms in graphene are connected by sp^2 hybrid bonds, enclosing an angle of 120°. The parent material of graphene is graphite, a stack of graphene sheets that are weakly bonded to each other. In fact, graphene can be isolated from graphite by peeling off flakes with a piece of scotch tape. In diamond, the carbon atoms form sp^3-type bonds and each atom has four nearest neighbors in a tetrahedral configuration. Interestingly, the diamond structure can also be described as an fcc Bravais lattice with a basis of two atoms.

The diamond structure is also found for Si and Ge. Many other isoelectronic materials (with the same total number of valence electrons), such as SiC, GaAs, and InP, also crystallize in a diamond-like structure but with each element on a different fcc sublattice.

1.3
Crystal Structure Determination

After having described different crystal structures, the question is of course how to determine these structures in the first place. By far, the most important technique for doing this is X-ray diffraction. In fact, the importance of this technique goes far beyond solid state physics, as it has become an essential tool for fields such as structural biology as well. There the idea is that, if you want to know the structure of a given protein, you can try to crystallize it and use the powerful methodology for structural determination by X-ray diffraction. We will also use X-ray diffraction as a motivation to extend our formal description of structures a bit.

1.3.1
X-Ray Diffraction

X-rays interact rather weakly with matter. A description of X-ray diffraction can therefore be restricted to single scattering, that is, incoming X-rays get scattered not more than once (most are not scattered at all). This is called the **kinematic approximation**; it greatly simplifies matters and is used throughout the treatment here. In addition to this, we will assume that the X-ray source and detector are very far away from the sample so that the incoming and outgoing waves can be treated as plane waves. X-ray diffraction of crystals was discovered and described by M. von Laue in 1912. Also in 1912, W. L. Bragg came up with an alternative description that is considerably simpler and serves as a starting point here.

1.3.1.1   Bragg Theory

Bragg treated the problem as the reflection of the incoming X-rays at flat crystal planes. These planes could, for example, be the close-packed planes making up the fcc and hcp crystals, or they could be alternating Cs and Cl planes making up the CsCl structure. At first glance, this has very little physical justification because the crystal planes are certainly not "flat" for X-rays that have a wavelength similar to the atomic spacing. Nevertheless, the description is highly successful, and we
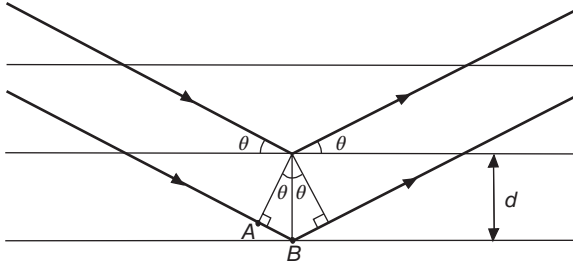
Figure 1.8 Construction for the derivation of the Bragg condition. The horizontal lines represent the crystal lattice planes that are separated by a distance *d*. The heavy lines represent the X-rays.

shall later see that it is actually a special case of the more complex Laue description of X-ray diffraction.

Figure 1.8 shows the geometrical considerations behind the Bragg description. A collimated beam of monochromatic X-rays hits the crystal. The intensity of diffracted X-rays is measured *in the specular direction*. The angle of incidence and emission is $90° - \Theta$. The condition for constructive interference is that the path length difference between the X-rays reflected from one layer and the next layer is an integer multiple of the wavelength λ. In the figure, this means that $2AB = n\lambda$, where AB is the distance between points A and B and n is a natural number. On the other hand, we have $\sin \theta = AB/d$ such that we arrive at the **Bragg condition**

$$n\lambda = 2d \sin \theta. \tag{1.3}$$

It is obvious that if this condition is fulfilled for one layer and the layer below, it will also be fulfilled for any number of layers with identical spacing. In fact, the X-rays penetrate very deeply into the crystal so that thousands of layers contribute to the reflection. This results into very sharp maxima in the diffracted intensity, similar to the situation for an optical grating with many lines. The Bragg condition can obviously only be fulfilled for $\lambda < 2d$, putting an upper limit on the wavelength of the X-rays that can be used for crystal structure determination.

1.3.1.2 Lattice Planes and Miller Indices

The Bragg condition will work not only for a special kind of lattice plane in a crystal, such as the hexagonal planes in an hcp crystal, but for all possible parallel planes in a structure. We therefore come up with a more stringent definition of the term **lattice plane**. It can be defined as a plane containing at least three non-collinear points of a given Bravais lattice. If it contains three, it will actually contain infinitely many because of translational symmetry. Examples for lattice planes in a simple cubic structure are shown in Figure 1.9.

The lattice planes can be characterized by a set of three integers, the so-called **Miller indices**. We arrive at these in three steps:

1) We find the intercepts of the plane with the crystallographic axes in units of the lattice vectors, for example, $(1, \infty, \infty)$ for the leftmost plane in Figure 1.9.
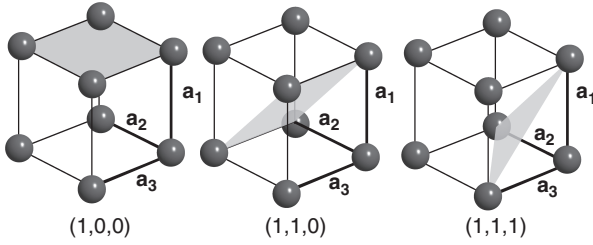
Figure 1.9 Three different lattice planes in the simple cubic structure characterized by their Miller indices.

2) We take the "reciprocal value" of these three numbers. For our example, this gives $(1, 0, 0)$.
3) By multiplying with some factor, we reduce the numbers to the smallest set of integers having the same ratio. This is not necessary in the example as we already have integer values.

Such a set of three integers can then be used to denote any given lattice plane. Later, we will encounter a different and more elegant definition of the Miller indices.

In practice, the X-ray diffraction peaks are so sharp that it is difficult to align and move the sample such that the incoming and reflected X-rays lie in one plane with the normal direction to a certain crystal plane. An elegant way to circumvent this problem is to use a powder of very small crystals instead of a large single crystal. This will not only ensure that some small crystals are orientated correctly to get constructive interference from a certain set of crystal planes, it will automatically give the interference pattern for all possible crystal planes.

1.3.1.3 General Diffraction Theory

The Bragg theory for X-ray diffraction is useful for extracting the distances between lattice planes in a crystal, but it has its limitations. Most importantly, it does not give any information on what the lattice actually consists of, that is, the basis. Also, the fact that the X-rays should be reflected by planes is physically somewhat obscure. We now discuss a more general description of X-ray diffraction that goes back to M. von Laue.

The physical process leading to X-ray scattering is that the electromagnetic field of the X-rays forces the electrons in the material to oscillate with the same frequency as that of the field. The oscillating electrons then emit new X-rays that give rise to an interference pattern. For the following discussion, however, it is merely important that something scatters the X-rays, not what it is.

It is highly beneficial to use the complex notation for describing the electromagnetic X-ray waves. For the electric field, a general plane wave can be written as

$$\boldsymbol{\mathcal{E}}(\mathbf{r}, t) = \boldsymbol{\mathcal{E}}_0 e^{i\mathbf{k}\cdot\mathbf{r} - i\omega t}. \tag{1.4}$$
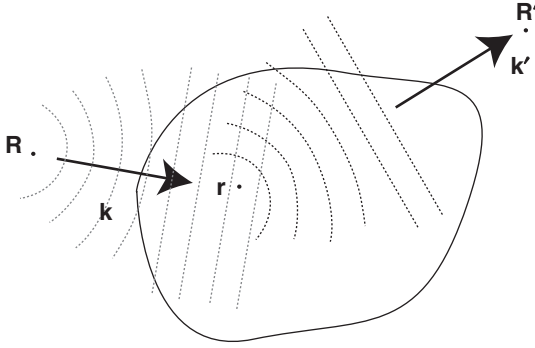
Figure 1.10 Illustration of X-ray scattering from a sample. The source and detector for the X-rays are placed at $\mathbf{R}$ and $\mathbf{R}'$, respectively. Both are very far away from the sample.

The wave vector $\mathbf{k}$ points in the direction of the wave propagation with a length of $2\pi/\lambda$, where λ is the wavelength. The convention is that the physical electric field is obtained as the real part of the complex field and the intensity of the wave is obtained as

$$I(\mathbf{r}) = |\mathcal{E}_0 e^{i\mathbf{k}\cdot\mathbf{r}-i\omega t}|^2 = |\mathcal{E}_0|^2. \tag{1.5}$$

Consider now the situation depicted in Figure 1.10. The source of the X-rays is far away from the sample at the position $\mathbf{R}$, so that the X-ray wave at the sample can be described as a plane wave. The electric field at a point $\mathbf{r}$ in the crystal at time t can be written as

$$\mathcal{E}(\mathbf{r}, t) = \mathcal{E}_0 e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R})-i\omega t}. \tag{1.6}$$

Before we proceed, we can drop the absolute amplitude $\mathcal{E}_0$ from this expression because we are only concerned with relative phase changes. The field at point $\mathbf{r}$ is then

$$\mathcal{E}(\mathbf{r}, t) \propto e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R})}e^{-i\omega t}. \tag{1.7}$$

A small volume element dV located at $\mathbf{r}$ will give rise to scattered waves in all directions. The direction of interest is the direction towards the detector that shall be placed at the position $\mathbf{R}'$, in the direction of a second wave vector $\mathbf{k}'$. We assume that the amplitude of the wave scattered in this direction will be proportional to the incoming field from (1.7) and to a factor $\rho(\mathbf{r})$ describing the scattering probability and scattering phase. We already know that the scattering of X-rays proceeds via the electrons in the material, and for our purpose, we can view $\rho(\mathbf{r})$ as the electron concentration in the solid. For the field at the detector, we obtain

$$\mathcal{E}(\mathbf{R}', t) \propto \mathcal{E}(\mathbf{r}, t)\rho(\mathbf{r})e^{i\mathbf{k}'\cdot(\mathbf{R}'-\mathbf{r})}. \tag{1.8}$$

Again, we have assumed that the detector is very far away from the sample such that the scattered wave at the detector can be written as a plane wave. Inserting (1.7) gives the field at the detector as

$$\mathcal{E}(\mathbf{R}', t) \propto e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R})}\rho(\mathbf{r})e^{i\mathbf{k}'\cdot(\mathbf{R}'-\mathbf{r})}e^{-i\omega t} = e^{i(\mathbf{k}'\cdot\mathbf{R}'-\mathbf{k}\cdot\mathbf{R})}\rho(\mathbf{r})e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}}e^{-i\omega t}. \tag{1.9}$$

We drop the first factor that does not contain **r** and will thus not play a role for the interference of X-rays emitted from different positions in the sample. The total wave field at the detector can finally be calculated by integrating over the entire volume of the crystal V. As the detector is far away from the sample, the wave vector **k**′ is essentially the same for all points in the sample. The result is

$$\mathcal{E}(\mathbf{R}', t) \propto e^{-i\omega t} \int_V \rho(\mathbf{r}) e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} dV. \tag{1.10}$$

In most cases, it will only be possible to measure the intensity of the X-rays, not the field, and this intensity is

$$I(\mathbf{K}) \propto \left| e^{-i\omega t} \int_V \rho(\mathbf{r}) e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} dV \right|^2 = \left| \int_V \rho(\mathbf{r}) e^{-i\mathbf{K}\cdot\mathbf{r}} dV \right|^2, \tag{1.11}$$

where we have introduced the so-called scattering vector $\mathbf{K} = \mathbf{k}' - \mathbf{k}$, which is just the difference of outgoing and incoming wave vectors. Note that although the direction of the wave vector for the scattered waves **k**′ is different from that of the incoming wave **k**, the length is the same because we only consider elastic scattering.

Equation (1.11) is the final result. It relates the measured intensity to the electron concentration in the sample. Except for very light elements, most of the electrons are located close to the ion cores and the electron concentration that scatters the X-rays is essentially identical to the geometrical arrangement of the ion cores. Hence, (1.11) can be used for the desired structural determination. To this end, one could try to measure the intensity as a function of scattering vector **K** and to infer the structure from the result. This is a formidable task. It is greatly simplified if the specimen under investigation is a crystal with a periodic lattice. In the following, we introduce the mathematical tools that are needed to exploit the crystalline structure in the analysis. The most important one is the so-called reciprocal lattice.

1.3.1.4   The Reciprocal Lattice

The concept of the reciprocal lattice is fundamental to solid state physics because it permits us to exploit the crystal symmetry for the analysis of many problems. Here we will use it to describe X-ray diffraction from periodic structures and we will meet it again and again in the next chapters. Unfortunately, the meaning of the reciprocal lattice turns out to be hard to grasp. Here, we choose to start out with a formal definition and we provide some mathematical properties. We then discuss the meaning of the reciprocal lattice before we come back to X-ray diffraction. The full importance of the concept will become apparent throughout this book.

For a given Bravais lattice

$$\mathbf{R} = m\mathbf{a_1} + n\mathbf{a_2} + o\mathbf{a_3}, \tag{1.12}$$

we define the reciprocal lattice as the set of vectors **G** for which

$$\mathbf{R} \cdot \mathbf{G} = 2\pi l, \tag{1.13}$$

where l is an integer. Equivalently, we could require that

$$e^{i\mathbf{G} \cdot \mathbf{R}} = 1. \tag{1.14}$$

Note that this equation must hold for *any* choice of the lattice vector $\mathbf{R}$ and reciprocal lattice vector $\mathbf{G}$. We can write any $\mathbf{G}$ as the sum of three vectors

$$\mathbf{G} = m'\mathbf{b_1} + n'\mathbf{b_2} + o'\mathbf{b_3}, \tag{1.15}$$

where m', n' and o' are integers. The reciprocal lattice is again a Bravais lattice. The vectors $\mathbf{b_1}$, $\mathbf{b_2}$, and $\mathbf{b_3}$ spanning the reciprocal lattice can be constructed explicitly from the lattice vectors

$$\mathbf{b_1} = 2\pi\frac{\mathbf{a_2} \times \mathbf{a_3}}{\mathbf{a_1} \cdot (\mathbf{a_2} \times \mathbf{a_3})}, \qquad \mathbf{b_2} = 2\pi\frac{\mathbf{a_3} \times \mathbf{a_1}}{\mathbf{a_1} \cdot (\mathbf{a_2} \times \mathbf{a_3})}, \qquad \mathbf{b_3} = 2\pi\frac{\mathbf{a_1} \times \mathbf{a_2}}{\mathbf{a_1} \cdot (\mathbf{a_2} \times \mathbf{a_3})}.$$
$$\tag{1.16}$$

From this, one can derive the simple but useful property,[1]

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}, \tag{1.17}$$

which can easily be verified. Equation (1.17) can then be used to verify that the reciprocal lattice vectors defined by (1.15) and (1.16) do indeed fulfill the fundamental property of (1.13) that defines the reciprocal lattice (see Problem 1.6).

Another way to view the vectors of the reciprocal lattice is as wave vectors that yield plane waves with the periodicity of the Bravais lattice because

$$e^{i\mathbf{G} \cdot \mathbf{r}} = e^{i\mathbf{G} \cdot \mathbf{r}} e^{i\mathbf{G} \cdot \mathbf{R}} = e^{i\mathbf{G} \cdot (\mathbf{r} + \mathbf{R})}. \tag{1.18}$$

Finally, one can define the **Miller indices** in a much simpler way using the reciprocal lattice: The Miller indices (i, j, k) define a plane that is perpendicular to the reciprocal lattice vector $i\mathbf{b_1} + j\mathbf{b_2} + k\mathbf{b_3}$ (see Problem 1.8).

1.3.1.5 The Meaning of the Reciprocal Lattice

We have now defined the reciprocal lattice in a proper way, and we will give some simple examples of its usefulness. The most important point of the reciprocal lattice is that it facilitates the description of functions that have the periodicity of the lattice. To see this, consider a one-dimensional lattice, a chain of points with a lattice constant a. We are interested in a function with the periodicity of the lattice, like the electron concentration along the chain $\rho(x) = \rho(x + a)$. We can write this as a Fourier series of the form

$$\rho(x) = C + \sum_{n=1}^{\infty} \left\{ C_n \cos(x 2\pi n/a) + S_n \sin(x 2\pi n/a) \right\} \tag{1.19}$$

with real coefficients C_n and S_n. The sum starts at $n = 1$, that is, the constant part C has to be taken out of the sum. We can also write this in a more compact form

$$\rho(x) = \sum_{n=-\infty}^{\infty} \rho_n e^{ixn2\pi/a}, \tag{1.20}$$

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1) δ_{ij} is Kronecker's delta, which is 1 for $i = j$ and zero otherwise.
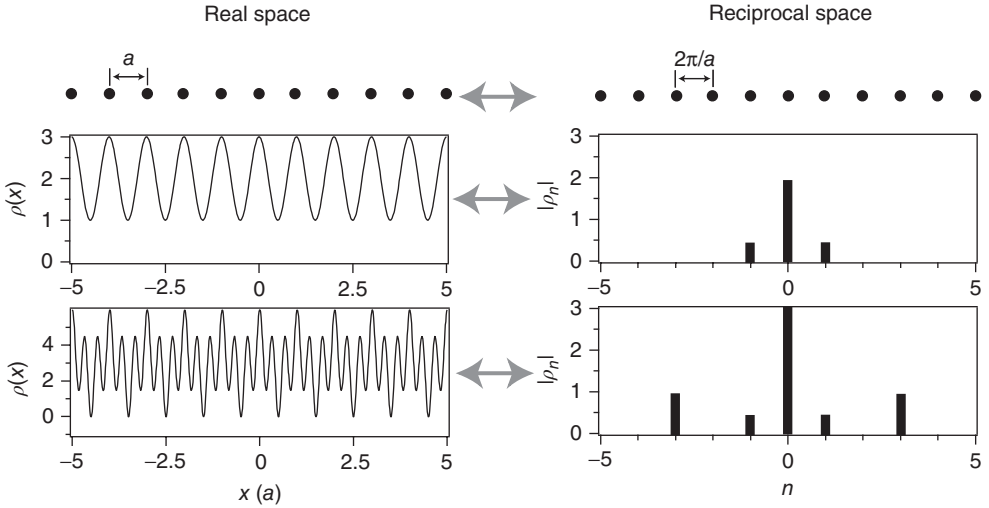
Figure 1.11   Top: Chain with a lattice constant a as well as its reciprocal lattice, a chain with a spacing of $2\pi/a$. Middle and bottom: Two lattice-periodic functions $\rho(x)$ in real space as well as their Fourier coefficients. The magnitude of the Fourier coefficients $|\rho_n|$ is plotted on the reciprocal lattice vectors they belong to.

using complex coefficients ρ_n. To ensure that $\rho(x)$ is still a real function, we have to require that

$$\rho^*_{-n} = \rho_n, \tag{1.21}$$

that is, that the coefficient ρ_{-n} must be the conjugate complex of the coefficient ρ_n. This description is more elegant than the one with the sine and cosine functions. How is it related to the reciprocal lattice? In one dimension, the reciprocal lattice of a chain of points with lattice constant a is also a chain of points with spacing $2\pi/a$ (see (1.17)). This means that we can write a general reciprocal lattice "vector" as

$$g = n\frac{2\pi}{a}, \tag{1.22}$$

where n is an integer. Exactly these reciprocal lattice "vectors" appear in (1.20). In fact, (1.20) is a sum of functions with a periodicity corresponding to the reciprocal lattice vectors, weighted by the coefficients ρ_n. Figure 1.11 illustrates these ideas by showing the lattice and reciprocal lattice for such a chain as well as two lattice-periodic functions, as real space functions and as Fourier coefficients on the reciprocal lattice points. The advantage of describing the functions by the coefficients ρ_n is immediately obvious: Instead of giving $\rho(x)$ for *every* point in a range of $0 \leqslant x < a$, the Fourier description consists only of three numbers for the upper function and five numbers for the lower function. Actually, it is only two and three numbers because of (1.21).

The same ideas also work in three dimensions. In fact, one can use a Fourier sum for lattice-periodic properties, which exactly corresponds to (1.20). For the

lattice-periodic electron concentration $\rho(\mathbf{r}) = \rho(\mathbf{r} + \mathbf{R})$, we get

$$\rho(\mathbf{r}) = \sum_{\mathbf{G}} \rho_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{r}}, \tag{1.23}$$

where $\mathbf{G}$ are the reciprocal lattice vectors.

With this we have seen that the reciprocal lattice is very useful for describing lattice-periodic functions. But this is not all: It can also simplify the treatment of waves in crystals in a very general sense. Such waves can be X-rays, elastic lattice distortions, or even electronic wave functions. We will come back to this point at a later stage.

1.3.1.6 X-Ray Diffraction from Periodic Structures

Turning back to the specific problem of X-ray diffraction, we can now exploit the fact that the electron concentration is lattice-periodic by inserting (1.23) in our expression (1.11) for the diffracted intensity. This gives

$$I(\mathbf{K}) \propto \left| \sum_{\mathbf{G}} \rho_{\mathbf{G}} \int_V e^{i(\mathbf{G}-\mathbf{K}) \cdot \mathbf{r}} dV \right|^2. \tag{1.24}$$

Let us inspect the integrand. The exponential function represents a plane wave with a wave vector $\mathbf{G} - \mathbf{K}$. If the crystal is very big, the integration will average over the crests and troughs of this wave and the result of the integration will be very small (or zero for an infinitely large crystal). The only exception to this is the case where

$$\mathbf{K} = \mathbf{k}' - \mathbf{k} = \mathbf{G}, \tag{1.25}$$

that is, when the difference between incoming and scattered wave vector is equal to a reciprocal lattice vector. In this case, the exponential function in the integral is 1, and the value of the integral is equal to the volume of the crystal. Equation (1.25) is often called the **Laue condition**. It is central to the description of X-ray diffraction from crystals in that it describes the condition for the observation of constructive interference.

Looking back at (1.24), the observation of constructive interference for a chosen scattering geometry (or scattering vector $\mathbf{K}$) clearly corresponds to a particular reciprocal lattice vector $\mathbf{G}$. The intensity measured at the detector is proportional to the square of the Fourier coefficient of the electron concentration $|\rho_{\mathbf{G}}|^2$. We could therefore think of measuring the intensity of the diffraction spots appearing for all possible reciprocal lattice vectors, obtaining the Fourier coefficients of the electron concentration and reconstructing this concentration. This would give all the information needed and conclude the process of the structural determination. Unfortunately, this straightforward approach does not work because the Fourier coefficients are complex, not real numbers. Taking the square root of the intensity at the diffraction spot therefore gives the magnitude but not the phase of $\rho_{\mathbf{G}}$. The phase is lost in the measurement. This is known as the **phase problem** in X-ray diffraction. One has to work around it to solve the structure. One simple approach is to calculate the electron concentration for a structural model, obtain

the magnitude of the $\rho_{\mathbf{G}}$ values and thus also the expected diffracted intensity, and compare this to the experimental result. Based on the outcome, the model can be refined until the agreement is satisfactory.

More precisely, this can be done in the following way. We start with (1.11), the expression for the diffracted intensity that we had obtained before introducing the reciprocal lattice. But now we know that constructive interference is only observed in a geometry that corresponds to fulfilling the Laue condition and we can therefore write the intensity for a particular diffraction spot as

$$I(\mathbf{G}) \propto \left| \int_V \rho(\mathbf{r}) e^{-i\mathbf{G}\cdot\mathbf{r}} dV \right|^2. \tag{1.26}$$

We also know that the crystal is made of many identical unit cells at the positions of the Bravais lattice $\mathbf{R}$. We can split the integral up as a sum of integrals over the individual unit cells

$$I(\mathbf{G}) \propto \left| \sum_{\mathbf{R}} \int_{V_{\text{cell}}} \rho(\mathbf{r} + \mathbf{R}) e^{-i\mathbf{G}\cdot(\mathbf{r}+\mathbf{R})} dV \right|^2 = \left| N \int_{V_{\text{cell}}} \rho(\mathbf{r}) e^{-i\mathbf{G}\cdot\mathbf{r}} dV \right|^2, \tag{1.27}$$

where N is the number of unit cells in the crystal and we have used the lattice periodicity of $\rho(\mathbf{r})$ and (1.14) in the last step. We now assume that the electron concentration in the unit cell $\rho(\mathbf{r})$ is given by the sum of atomic electron concentrations $\rho_i(\mathbf{r})$ that can be calculated from the atomic wave functions. By doing so, we neglect the fact that some of the electrons form the bonds between the atoms and are not part of the spherical electron cloud around the atom any longer. If the atoms are not too light, however, the number of these valence electrons is small compared to the total number of electrons and the approximation is appropriate. We can then write

$$\rho(\mathbf{r}) = \sum_i \rho_i(\mathbf{r} - \mathbf{r}_i), \tag{1.28}$$

where we sum over the different atoms in the unit cell at positions $\mathbf{r}_i$. This permits us to rewrite the integral in (1.27) as a sum of integrals over the individual atoms in the unit cell

$$\int_{V_{\text{cell}}} \rho(\mathbf{r}) e^{-i\mathbf{G}\cdot\mathbf{r}} dV = \sum_i e^{-i\mathbf{G}\cdot\mathbf{r}_i} \int_{V_{\text{atom}}} \rho_i(\mathbf{r}') e^{-i\mathbf{G}\cdot\mathbf{r}'} dV', \tag{1.29}$$

where $\mathbf{r}' = \mathbf{r} - \mathbf{r}_i$. The two exponential functions give rise to two types of interference. The first describes the interference between the X-rays scattered by the different atoms in the unit cell, and the second the interference between the X-rays scattered by the electrons within one atom. The last integral is called the **atomic form factor** and can be calculated from the atomic properties alone. We therefore see how the diffracted intensity for an assumed structure can be calculated from the atomic form factors and the arrangement of the atoms.

1.3.1.7 The Ewald Construction

In 1913, P. Ewald published an intuitive geometrical construction to visualize the Laue condition (1.25) and to determine the directions $\mathbf{k}'$ for which constructive
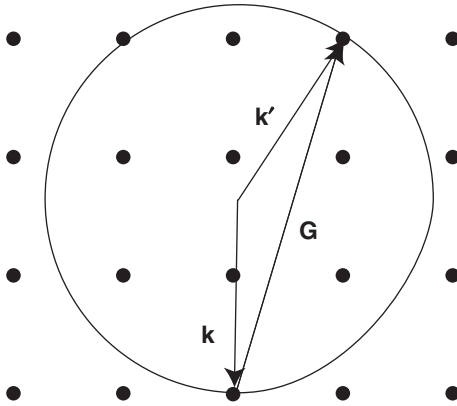
Figure 1.12 Ewald construction for finding the directions in which constructive interference can be observed. The dots represent the reciprocal lattice. The arrows labeled **k** and **k′** are the wave vectors of the incoming and scattered X-rays, respectively.

interference is to be expected. The construction is shown in Figure 1.12, which represents a cut through the reciprocal lattice; the black points are the reciprocal lattice points. The construction works as follows:

1) We draw the wave vector **k** of the incoming X-rays such that it ends in the origin of the reciprocal lattice (we may of course choose the point of origin freely).
2) We construct a circle of radius |**k**| around the starting point of **k**.
3) Wherever the circle touches a reciprocal lattice point, the Laue condition **k′** − **k** = **G** is fulfilled.

For a three-dimensional crystal, this construction has to be carried out in different planes, of course. The figure clearly shows that (1.25) is a very stringent condition: It is not likely for the sphere to hit a second reciprocal lattice point, so that constructive interference is only expected for very few directions. As in the Bragg description, we see that the wavelength of the X-rays has to be short enough (|**k**| has to be long enough) for any constructive interference to occur.

Practical X-ray diffraction experiments are often carried out in such a way that many constructive interference maxima are observed despite the strong restrictions imposed by the Laue condition (1.25). This can, for example, be achieved by using a wide range of X-ray wavelengths, that is, non monochromatic radiation or by doing diffraction experiments not on one single crystal but on a powder of randomly oriented small crystals.

1.3.1.8 Relation Between Bragg and Laue Theory

We conclude our treatment of X-ray diffraction by showing that the Bragg description of X-ray diffraction is just a special case of the Laue description. We start by noting that the Laue condition (1.25) consists, in fact, of three separate conditions for the three components of the vectors. In the Bragg experiment, two of these

conditions are automatically fulfilled because of the specular geometry: The wave vector change parallel to the lattice planes is zero. So, the vector equation (1.25) reduces to the scalar equation

$$k'_\perp - k_\perp = 2k_\perp = 2\frac{2\pi}{\lambda}\sin\Theta = G_\perp, \tag{1.30}$$

where $G_\perp$ is a reciprocal lattice vector perpendicular to the lattice planes. We have seen in Section 1.3.1.4 that such a reciprocal lattice vector exists for any set of planes. The planes can be defined by their Miller indices (i, j, k) or by the reciprocal lattice vector $\mathbf{G}_\perp = i\mathbf{b_1} + j\mathbf{b_2} + k\mathbf{b_3}$ that is perpendicular to the planes (see Problem 1.8). The shortest possible $\mathbf{G}_\perp$ has a length of $2\pi/d$ with d being the distance between the planes, but any integer multiple of this will also work. If we thus insert $m2\pi/d$ for $G_\perp$ into (1.30), we obtain the usual form of the Bragg condition (1.3).

1.3.2
Other Methods for Structural Determination

While X-ray diffraction is arguably the most widespread and powerful method for structural determination, other techniques are used as well. Similar diffraction experiments can be carried out by making use of the wave character of neutrons or electrons. The former interact very weakly with matter because they are charge-neutral. They are also more difficult to produce than X-rays. However, the use of neutrons has two distinct advantages over X-rays: First, that their relative interaction strength with light atoms is stronger and second, that they carry a magnetic moment. They can therefore interact with the magnetic moments in the solid, that is, one can determine the magnetic order. Electrons, on the other hand, have the advantages that they are easy to produce and that one can use electron-optical imaging techniques, whereas making optical elements for X-rays is very difficult. On the other hand, their very strong interaction with matter causes a breakdown of the kinematic approximation, that is, multiple scattering events have to be taken into account. Because of the strong interaction with matter, low-energy electrons do not penetrate deeply into crystals either. Therefore, they are more appropriate for surface structure determination.

1.3.3
Inelastic Scattering

Our discussion has been confined to the case of elastic scattering. In real experiments, however, the X-rays or particles can also lose energy during the scattering events. This can be described formally by considering the diffraction from a structure that does not consist of ions at fixed positions but is time-dependent, that is, which fluctuates with the frequencies of the atomic vibrations. We cannot go into the details of inelastic scattering processes here, but it is important to emphasize that the inelastic scattering, especially of neutrons, can be used to measure the vibrational properties of a lattice.

1.4
Further Reading

The concepts of lattice-periodic solids, crystal structure, and X-ray diffraction are discussed in all standard texts on solid state physics, for example,

- Ashcroft, N.W. and Mermin, N.D. (1976) *Solid State Physics*, Holt-Saunders.
- Ibach, H. and Lüth, H. (2009) *Solid State Physics*, 4th edn, Springer.
- Kittel, C. (2005) *Introduction to Solid State Physics*, 8th edn, John Wiley & Sons, Inc.
- Rosenberg, H.M. (1988) *The Solid State*, 3rd edn, Oxford University Press.

For a more detailed discussion of X-ray diffraction, see, for example,

- Als-Nielsen, J. and McMorrow, D. (2011) *Elements of Modern X-Ray Physics*, 2nd edn, John Wiley & Sons, Ltd.

1.5
Discussion and Problems

Discussion

1) What mathematical concepts do you need to describe the structure of any crystal?
2) What are typical crystal structures for metals and why?
3) Why do covalent crystals typically have a much lower packing density than metal crystals?
4) How can the reciprocal lattice conveniently be used to describe lattice-periodic functions?
5) How can you determine the structure of crystals?
6) What is the difference between the Bragg and von Laue descriptions of X-ray diffraction?
7) How can you use the reciprocal lattice of a crystal to predict the pattern of diffracted X-rays?

Problems

1) *Fundamental concepts:* In the two-dimensional crystal in Figure 1.13, find (a) the Bravais lattice and a primitive unit cell, (b) a nonprimitive, rectangular unit cell, and (c) the basis.
2) *Real crystal structures:* Show that the packing of spheres in a simple cubic lattice fills 52% of available space.
3) *Real crystal structures*: Figure 1.14 shows the structure for a two-dimensional hexagonal packed layer of atoms, a hcp crystal, a two-dimensional sheet of carbon atoms arranged in a honeycomb lattice (graphene), and three-dimensional graphite. (a) Draw a choice of vectors spanning the Bravais
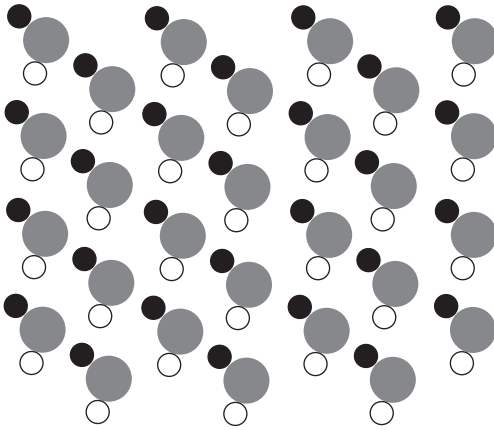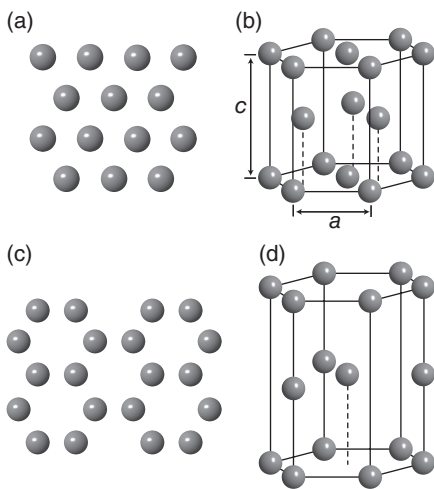
Figure 1.13   A two-dimensional crystal.

Figure 1.14   (a) Two-dimensional crystal structure of a hexagonal close-packed layer of atoms. (b) Crystal structure for a three-dimensional hcp crystal. (c) Two-dimensional crystal structure for graphene.

(d) Three-dimensional crystal structure for graphite (strongly compressed along the *c* direction). The lines are a mere guide to the eye, not indicating bonds or the size of the unit cell.

lattice for the hexagonal layer of atoms and for graphene, and compare them to each other. (b) Show that the basis for the hexagonal layer contains one atom, while the bases for graphene and the three-dimensional hcp crystal contain two atoms. (c) (*) Choose the vectors for the Bravais lattice for graphite and show that the basis contains four atoms.

4) *Real crystal structures:* Consider the hcp lattice shown in Figure 1.14b. The Bravais lattice underlying the hcp structure is given by two vectors of length a in one plane, with an angle of 60° between them and a third vector of length c perpendicular to that plane. There are two atoms per unit cell. (a) Show that for the ideal packing of spheres, the ratio $c/a = (8/3)^{1/2}$. (b) (*) Construct the reciprocal lattice. Does the fact that there are two atoms per unit cell in the hcp crystal have any relevance? Hint: Use the result of Problem 1.7.

5) *X-ray diffraction:* (a) Determine the maximum wavelength for which constructive interference can be observed in the Bragg model for a simple cubic crystal with a lattice constant of 3.6 Å. (b) What is the energy of the X-rays in electron volts? (c) If you were to perform neutron diffraction, what would the energy of the neutrons have to be in order to obtain the same de Broglie wavelength? (d) You could argue that if you take X-rays with twice the wavelength, you would still get a Bragg peak because there would be constructive interference between the X-rays that are reflected from every other plane. Why is this argument not valid? (e) You could describe the same crystal by using a unit cell that is a bigger cube of twice the side length, containing eight atoms instead of one. The lattice constant would then be 7.2 Å. Discuss how this different description would affect the X-ray diffraction from the crystal.

6) *The reciprocal lattice:* Using the explicit definition of the reciprocal lattice (1.16), show first that (1.17) is fulfilled and then, using this relation, show that the reciprocal lattice defined by (1.16) does indeed fulfill the condition (1.13).

7) *The reciprocal lattice:* For a two-dimensional Bravais lattice

$$\mathbf{R} = m\mathbf{a_1} + n\mathbf{a_2}, \tag{1.31}$$

the reciprocal lattice is also two-dimensional:

$$\mathbf{G} = m'\mathbf{b_1} + n'\mathbf{b_2}. \tag{1.32}$$

Often, the most practical way to construct the reciprocal lattice is to use the relation

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}, \tag{1.33}$$

which remains valid in the two-dimensional case. Find the reciprocal lattice for the three cases given in Figure 1.15.
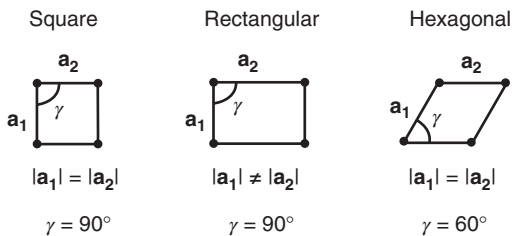

Figure 1.15 Two-dimensional Bravais lattices.

8) *Miller indices:* We have stated that the reciprocal lattice vector $m\mathbf{b_1} + n\mathbf{b_2} + o\mathbf{b_3}$ is perpendicular to the lattice plane given by the Miller indices (m, n, o). (a) Verify that this is correct for the lattice planes drawn in Figure 1.9. (b) (*) Show that this is true in general.