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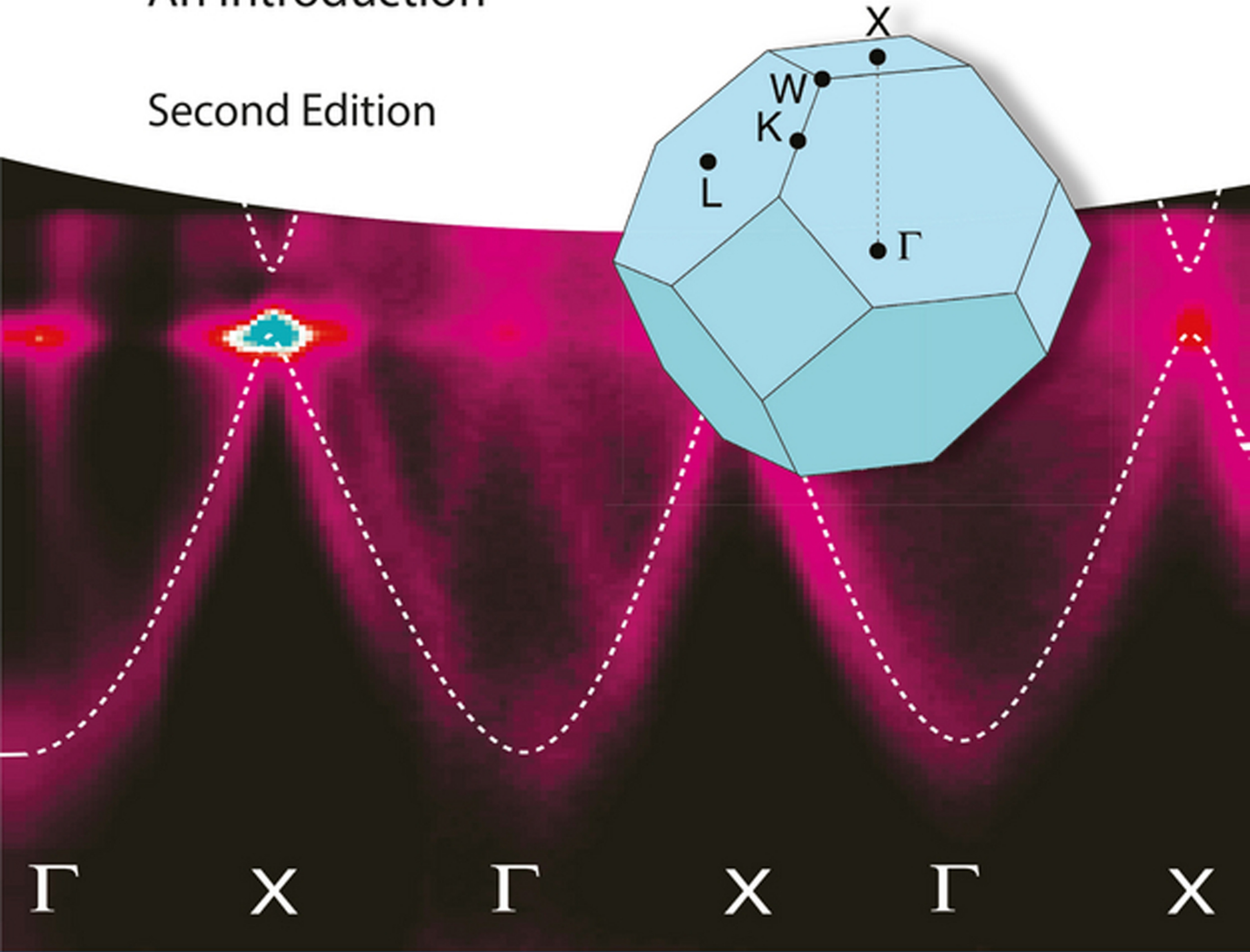
Philip Hofmann

Solid State Physics

An Introduction

Second Edition



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Solid State Physics

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The Author

Dr. Philip Hofmann
Department of Physics and Astronomy
Aarhus University
Ny Munkegade 120
8000 Aarhus C
Denmark

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Contents

Preface of the First Edition

This book emerged from a course on solid state physics for third-year students of physics and nanoscience, but it should also be useful for students of related fields such as chemistry and engineering. The aim is to provide a bachelor-level survey over the whole field without going into too much detail. With this in mind, a lot of emphasis is put on a didactic presentation and little on stringent mathematical derivations or completeness. For a more in-depth treatment, the reader is referred to the many excellent advanced solid state physics books. A few are listed in the Appendix.

To follow this text, a basic university-level physics course is required as well as some working knowledge of chemistry, quantum mechanics, and statistical physics. A course in classical electrodynamics is of advantage but not strictly necessary.

Some remarks on *how to use this book*: Every chapter is accompanied by a set of ”discussion” questions and problems. The intention of the questions is to give the student a tool for testing his/her understanding of the subject. Some of the questions can only be answered with knowledge of later chapters. These are marked by an asterisk. Some of the problems are more of a challenge in that they are more difficult mathematically or conceptually or both. These problems are also marked by an asterisk. Not all the information necessary for solving the problems is given here. For standard data, for example, the density of gold or the atomic weight of copper, the reader is referred to the excellent resources available on the World Wide Web.

Finally, I would like to thank the people who have helped me with many discussions and suggestions. In particular, I would like to mention my colleagues Arne Nylandsted Larsen, Ivan Steensgaard, Maria Fuglsang Jensen, Justin Wells, and many others involved in teaching the course in Aarhus.

Preface of the Second Edition

The second edition of this book is slightly enlarged in some subject areas and significantly improved throughout. The enlargement comprises subjects that turned out to be too essential to be missing, even in a basic introduction such as this one. One example is the tight-binding model for electronic states in solids, which is now added in its simplest form. Other enlargements reflect recent developments in the field that should at least be mentioned in the text and explained on a very basic level, such as graphene and topological insulators.

I decided to support the first edition by online material for subjects that were either crucial for the understanding of this text, but not familiar to all readers, or not central enough to be included in the book but still of interest. This turned out to be a good concept, and the new edition is therefore supported by an extended number of such notes; they are referred to in the text. The notes can be found on my homepage www.philiphofmann.net.

The didactical presentation has been improved, based on the experience of many people with the first edition. The most severe changes have been made in the chapter on magnetism but minor adjustments have been made throughout the book. In these changes, didactic presentation was given a higher priority than elegance or conformity to standard notation, for example, in the figures on Pauli paramagnetism or band ferromagnetism.

Every chapter now contains a "Further Reading" section in the end. Since these sections are supposed to be independent of each other, you will find that the same books are mentioned several times.

I thank the many students and instructors who participated in the last few years' Solid State Physics course at Aarhus University, as well as many colleagues for their criticism and suggestions. Special thanks go to NL architects for permitting me to use the flipper-bridge picture in Figure 11.3, to Justin Wells for suggesting the analogy to the topological insulators, to James Kermode for Figure 3.7, to Arne Nylandsted Larsen and Antonija Grubišić Čabo for advice on the sections on solar cells and magnetism, respectively.

Physical Constants and Energy Equivalents

Planck constant	h	$6.6260755 \times 10^{-34}$ J s $4.13566743 \times 10^{-15}$ eV s
Boltzmann constant	k_B	1.380658×10^{-23} J K^{-1} 8.617385×10^{-5} eV K^{-1}
Proton charge	e	$1.60217733 \times 10^{-19}$ C
Bohr radius	a_0	5.29177×10^{-11} m
Bohr magneton	μ_B	$9.2740154 \times 10^{-24}$ J T^{-1}
Avogadro number	N_A	6.0221367×10^{23} particles/mol
Speed of light	c	2.99792458×10^{8} m s^{-1}
Rest mass of the electron	m_e	$9.1093897 \times 10^{-31}$ kg
Rest mass of the proton	m_p	$1.6726231 \times 10^{-27}$ kg
Rest mass of the neutron	m_n	$1.6749286 \times 10^{-27}$ kg
Atomic mass unit	amu	1.66054×10^{-27} kg
Permeability of vacuum	μ_0	$4\pi \times 10^{-7}$ V s A^{-1}m^{-1}
Permittivity of vacuum	ϵ_0	$8.854187817 \times 10^{-12}$ C^2 J^{-1} m^{-1}

1 eV = $1.6021773 \times 10^{-19}$ J
1 K = 8.617385×10^{-5} eV

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.

Solid State Physics: An Introduction, Second Edition. Philip Hofmann.

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 $\mathbf{R}$, 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

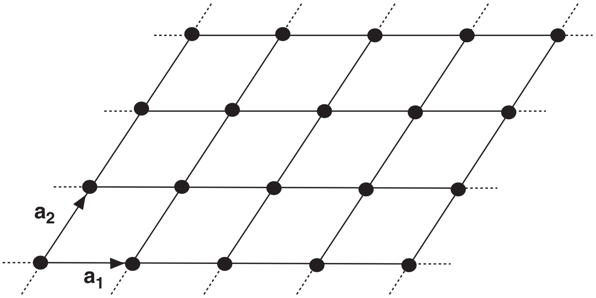

Figure 1.1 Example for a two-dimensional Bravais lattice.

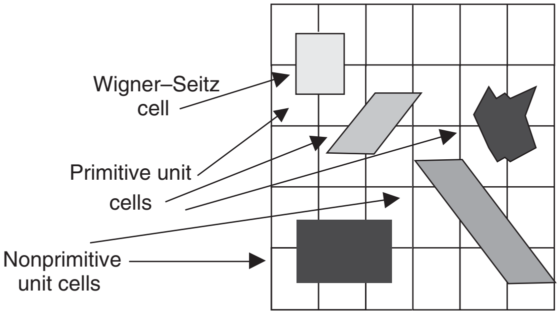

Figure 1.2 Illustration of unit cells (primitive and nonprimitive) and of the Wigner–Seitz cell for a rectangular two-dimensional lattice.

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.

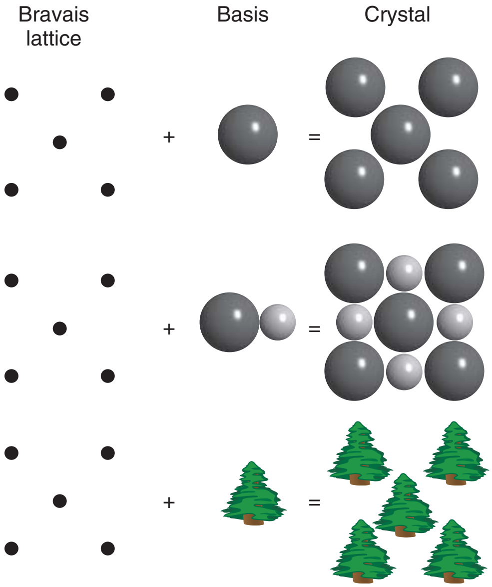

Figure 1.3 A two-dimensional Bravais lattice with different choices for the basis.

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.

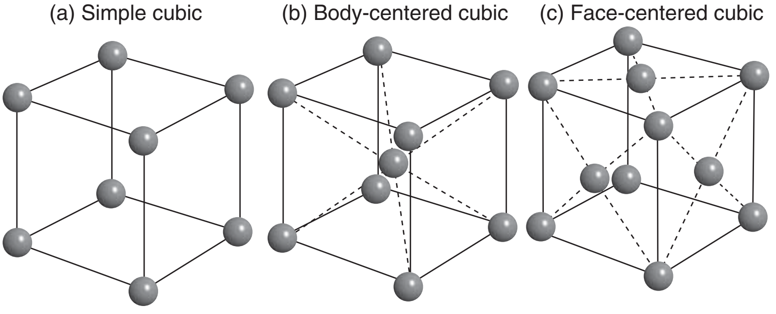

Figure 1.4 (a) Simple cubic structure; (b) body-centered cubic structure; and (c) face-centered cubic structure. Note that the spheres are depicted much smaller than in the situation of most dense packing and not all of the spheres on the faces of the cube are shown in (c).

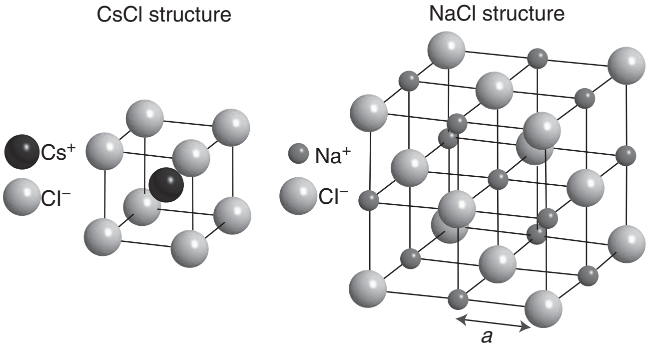

Figure 1.5 Structures of CsCl and NaCl. The spheres are depicted much smaller than in the situation of most dense packing, but the relative size of the different ions in each structure is correct.

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

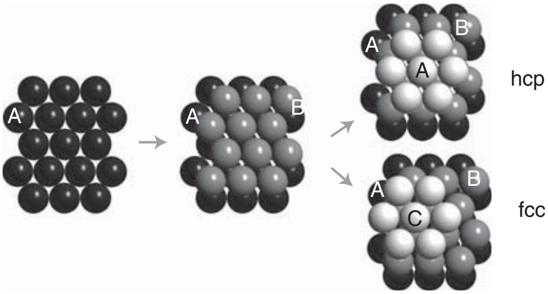

Figure 1.6 Close packing of spheres leading to the hcp and fcc structures.

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

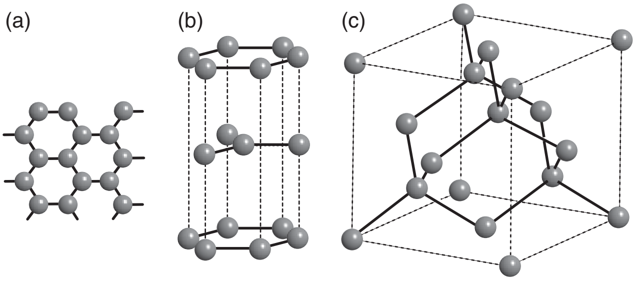

Figure 1.7 Structures for (a) graphene, (b) graphite, and (c) diamond. sp^2 and sp^3 bonds are displayed as solid lines.

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

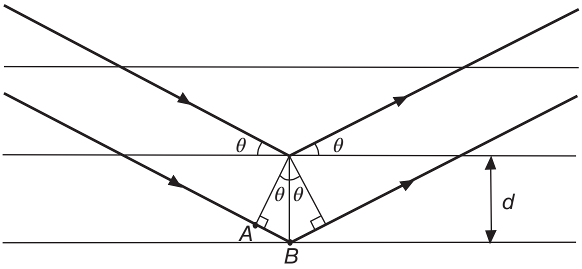

Figure 1.8 Construction for the derivation of the Bragg condition. The horizontal lines represent the crystal lattice planes that are separated by a distance *d*. The heavy lines represent the X-rays.

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 $90^\circ - \Theta$. 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 noncollinear 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.

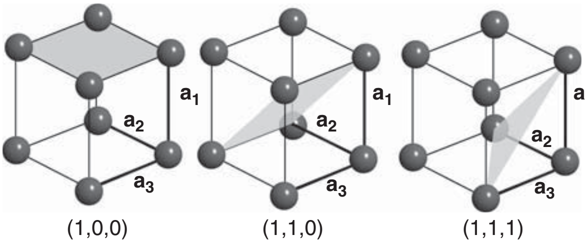

Figure 1.9 Three different lattice planes in the simple cubic structure characterized by their Miller indices.

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

$$\mathcal{E}(\mathbf{r}, t) = \mathcal{E}_0 e^{i\mathbf{k}\cdot\mathbf{r} - i\omega t}. \tag{1.4}$$