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Philip Hofmann

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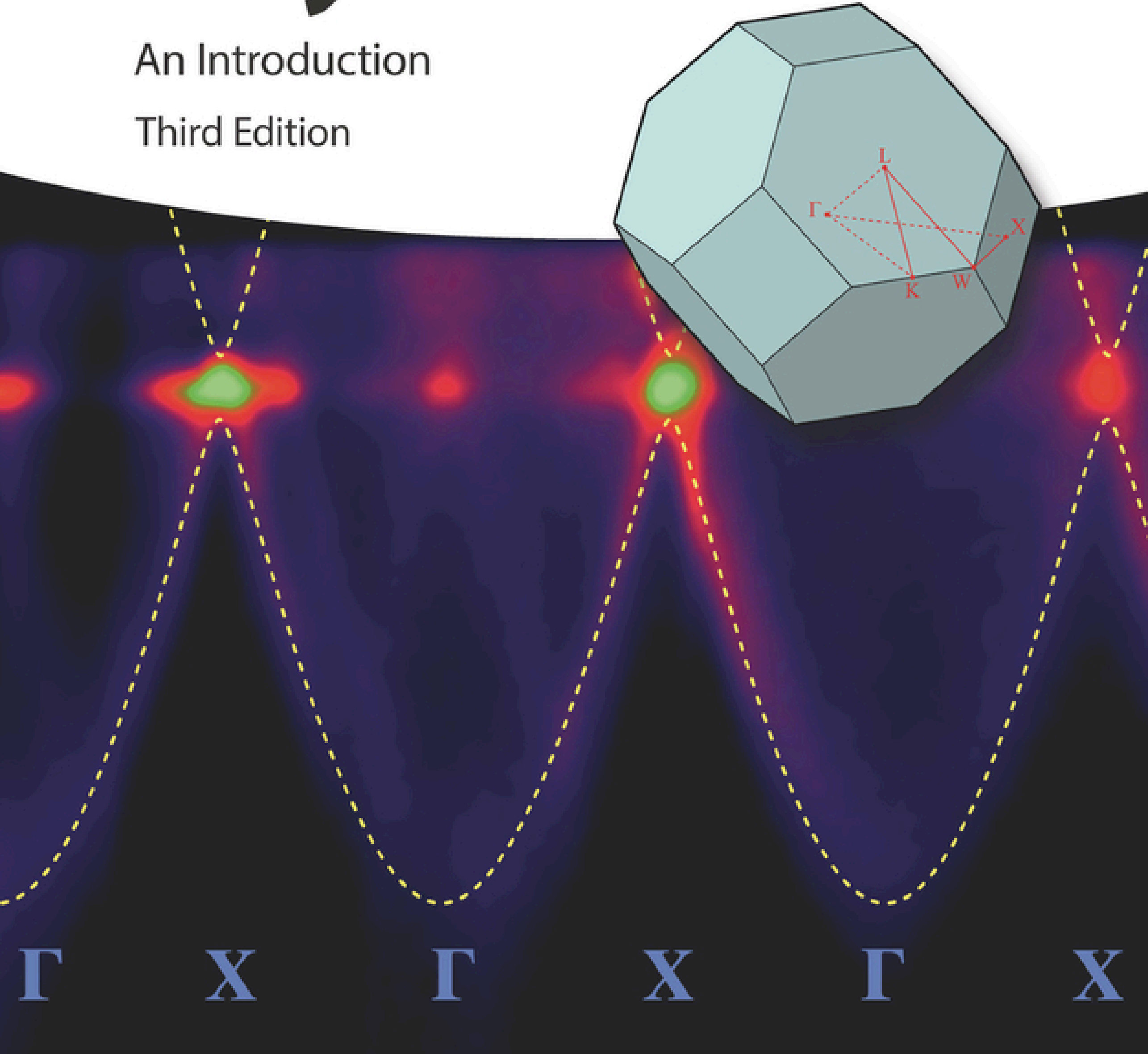
An Introduction

Third Edition



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Contents

Preface to 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 to the Second Edition

The second edition of this book is slightly enlarged in some subject areas and 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 website www.philiphofmann.net.

The didactic 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 at 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, and to Arne Nylandsted Larsen and Antonija Grubišić Čabo for advice on the sections on solar cells and magnetism, respectively.

Preface to the Third Edition

The third edition of this book introduces numerous improvements throughout the text, in particular in the description of covalent bonding in Chapter 2 and in the discussion of the Bloch theorem and the nearly-free electron model in Chapter 6.

The most significant changes are related to the problem sections in each chapter. In addition to the "traditional" type of problems that require an analytical solution, I have now included a number of problems that need to be solved numerically. Their complexity varies from plotting a simple function to calculating the carrier densities in a semiconductor. By introducing this new type of problems I hope to strengthen the students' computational skills, to overcome the restriction of being able to calculate solely what can be approximated using a simple model, and to impart upon students the capability to "play" with model parameters in order to explore what might happen in different physical situations. Moreover, exercises such as 4.4 and 6.10 are intended to help students understand the way phonon dispersions or electronic states are plotted as one-dimensional cuts through a multi-dimensional Brillouin zone. For instructors, Python scripts for individual problems are provided as part of the instructor resources that are available from the publisher.

Another major change in the problem sections is the addition of a "basic concepts" section in addition to the "discussion questions" and the more complex "problems" from the second edition. Many (but not all) of the new "basic concepts" questions are of the multiple-choice type and the solutions to all of them are given in Appendix B. As in the first two editions, the "discussion questions" can serve as an inspiration to think about the central new concepts of each chapter or for discussing them in class, whereas the "problems" serve for a more in-depth exploration of the subjects. As in the previous editions, problems marked by an asterisk * are particularly challenging. The "basic concepts" section can be used in self-studies to test one's understanding of the most important ideas. Most of the questions do not require any calculations but they still go beyond a simple repetition of the chapter's content and involve some thinking. The number of "basic concepts" questions in a given chapter depends on the number and complexity of new concepts introduced in this chapter. Chapter 1, for instance, introduces difficult and very important ideas such as the reciprocal lattice, and therefore it contains a large number of "basic concepts" questions. Chapter 3, on the other hand, is conceptually less difficult and contains only a few of them. Many more of this type of questions along with their solutions can be found on my website at www.philiphofmann.net.

The multiple-choice questions have only one correct answer, or, if several correct answers exist, there is an explicit option to choose this, e. g., “C. Both A. and B. are correct.” In some cases, there is an overlap between a “basic concepts” question testing a conceptual understanding of a subject and a “problem” with a more in-depth treatment of the same question.

My thanks go to the 2021 class of the Statistical Physics and Solid State Physics course at Aarhus University for testing much of the new content, as well as to the teaching instructors Paulina Majchrzak, Alfred Jones, Michael Iversen and Nikolaj Rønne. I also thank Davide Curcio for introducing me to a new set of advanced writing tools and Charlotte E. Sanders for many helpful comments on the manuscript.

Physical Constants and Energy Equivalents

Planck constant	h	$6.626\ 070\ 15 \times 10^{-34}\ \mathrm{J\,s}$
		$4.135\ 667\ 70 \times 10^{-15}\ \mathrm{eV\,s}$
Boltzmann constant	k_B	$1.380\ 649 \times 10^{-23}\ \mathrm{J\,K^{-1}}$
		$8.617\ 333 \times 10^{-5}\ \mathrm{eV\,K^{-1}}$
Proton charge	e	$1.602\ 176\ 63 \times 10^{-19}\ \mathrm{C}$
Bohr radius	a_0	$5.291\ 77 \times 10^{-11}\ \mathrm{m}$
Bohr magneton	μ_B	$9.274\ 010\ 1 \times 10^{-24}\ \mathrm{J\,T^{-1}}$
Avogadro constant	N_A	$6.022\ 140\ 8 \times 10^{23}\ \mathrm{mol^{-1}}$
Speed of light	c	$2.997\ 924\ 58 \times 10^{8}\ \mathrm{m\,s^{-1}}$
Rest mass of the electron	m_e	$9.109\ 383\ 7 \times 10^{-31}\ \mathrm{kg}$
Rest mass of the proton	m_p	$1.672\ 621\ 9 \times 10^{-27}\ \mathrm{kg}$
Rest mass of the neutron	m_n	$1.674\ 927\ 5 \times 10^{-27}\ \mathrm{kg}$
Atomic mass unit	u	$1.660\ 539 \times 10^{-27}\ \mathrm{kg}$
Permeability of vacuum	μ_0	$4\pi \times 10^{-7}\ \mathrm{V\,s\,A^{-1}m^{-1}}$
Permittivity of vacuum	ε_0	$8.854\ 187\ 813 \times 10^{-12}\ \mathrm{C^2\,J^{-1}\,m^{-1}}$

$1\ \mathrm{eV} = 1.602\ 176\ 634 \times 10^{-19}\ \mathrm{J}$

$1\ \mathrm{K} = 8.617\ 333 \times 10^{-5}\ \mathrm{eV}$

1

Crystal Structures

Our general objective in this book is to understand the macroscopic properties of solids on a microscopic level. 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) of the particles. 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 vast number of particles involved. In a way, this situation is similar to atomic physics where the key to a quantum-mechanical description is the spherical symmetry of the atom. We will often imagine a macroscopic solid as one **single crystal**, a perfect lattice of atoms without any defects whatsoever. While it may seem that such perfect crystals are not particularly relevant for real materials, this is in fact not the case. Many solids are actually composed of small crystalline grains. Such solids are called **polycrystalline**, in contrast to a macroscopic single crystal, but the number of atoms within a perfect crystalline environment in them 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 all atoms are at the grain boundaries.

There are, however, also solids that are not crystalline. These are called **amorphous**. The amorphous state is characterized by the absence of any long-range order. There may exist, however, a degree of 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. For the moment, we will not ask *why* the atoms bind together in the way they do – this topic will be discussed in Chapter 2. Finally, we delve into a 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, Third 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 non-collinear 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 corresponding 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 with different symmetries 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**. By this we denote any volume of space that, when translated through all the vectors of the Bravais lattice, will fill space without overlap and without leaving any voids. The primitive unit cell of a lattice contains only one lattice point. It is also possible to define **nonprimitive unit cells** containing 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 illustrated in Figure 1.2. It is evident from the figure 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**, which 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 describes the items we “put” on the lattice points, that is, the building blocks for the real crystal. The basis can consist of one or several atoms, or even of complex molecules as in the case of protein crystals. Different cases are illustrated in Figure 1.3.

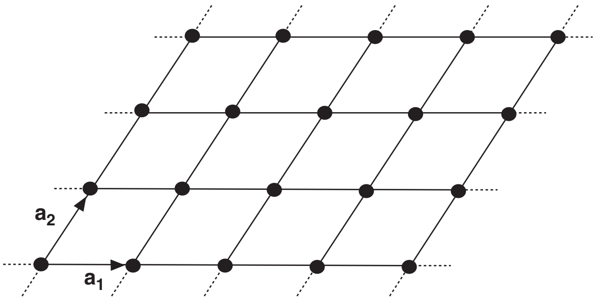


Figure 1.1 A two-dimensional Bravais lattice.

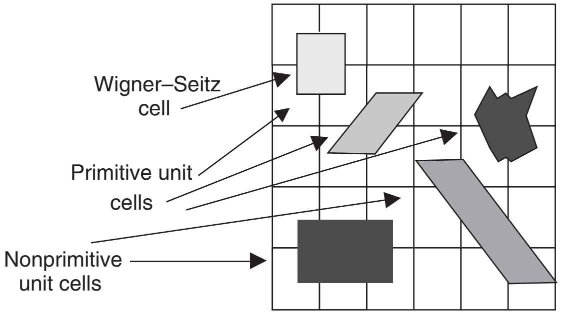


Figure 1.2 Illustration of (primitive and nonprimitive) unit cells and of the Wigner–Seitz cell for a rectangular two-dimensional lattice.

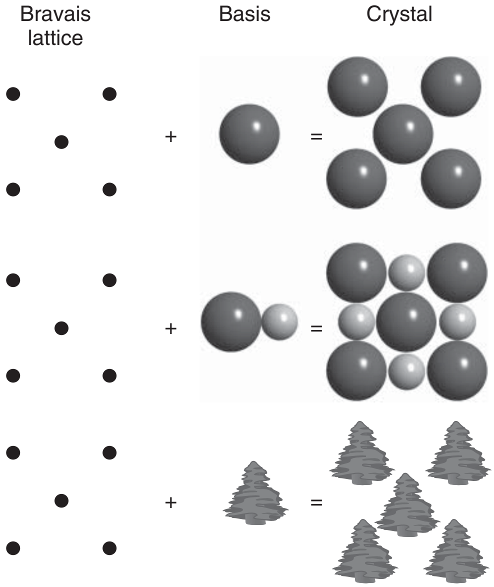


Figure 1.3 A two-dimensional Bravais lattice with different choices for the basis.

Finally, we add a remark about symmetry. So far, we discussed only **translational symmetry**. However, a real crystal may also exhibit **point symmetry**. Compare the structures in the middle and the bottom of Figure 1.3. The former structure possesses a number of symmetry elements that are missing in the latter – 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.

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 Chapter 2, we will take a closer look at the details of the bonding in these types of solids.

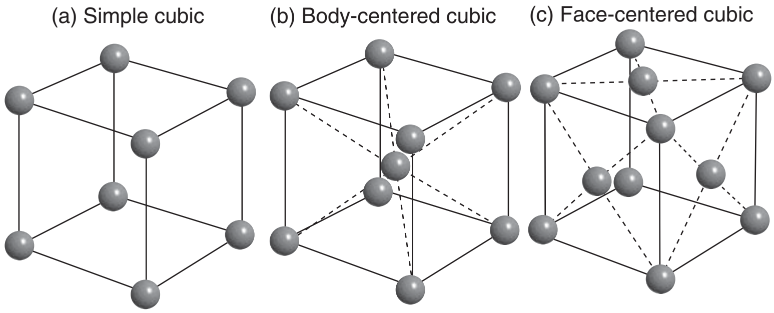


Figure 1.4 (a) Simple cubic structure; (b) body-centered cubic structure; and (c) face-centered cubic structure. Note that the spheres are depicted much smaller than in the situation of most dense packing and not all of the spheres on the faces of the cube are shown in (c).

1.2.1 Cubic Structures

We begin with one of the simplest crystal structures possible, 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 understanding many other structures. Only one chemical element (polonium) is found to crystallize in the simple cubic structure. The structure is unfavorable because of its openness – there are many voids, if we think of the atoms as solid spheres in contact with each other. In metals, which are the most common elemental solids, directional bonding is not important, and a close packing of the atoms is usually favored. We will learn more about this in the next chapter. For covalent solids, on the other hand, directional bonding *is* important, but six bonds extending from the same atom in an octahedral configuration is highly uncommon 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 depicted in Figure 1.4. In fact, the fcc structure has the highest possible packing density for identical spheres, as we shall see later. These two structures are very common – 17 elements crystallize in the bcc structure and 24 elements in the fcc structure. Note that the simple cubic structure ist the only one for which the cube is identical with the Bravais lattice. While the cube is also a unit cell for the bcc and fcc lattices, ist it not the primitive unit cell in these cases. Still, 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.

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, which 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 positive and negative ions.

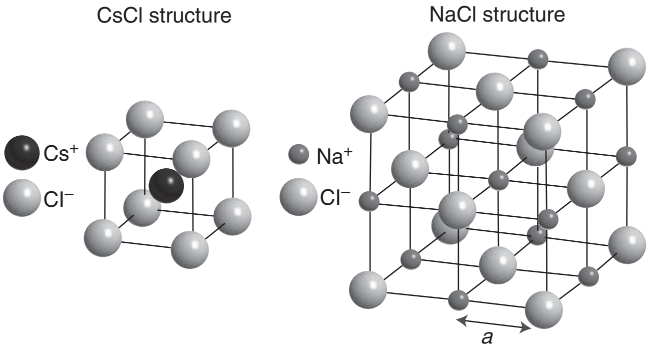
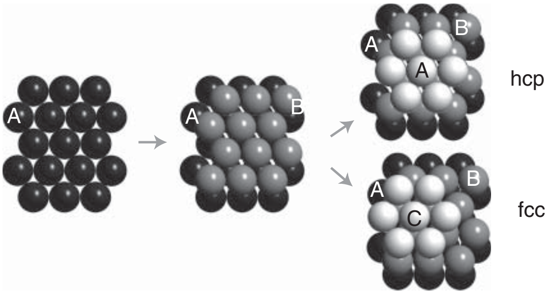


Figure 1.5 Structures of CsCl and NaCl. The spheres are depicted much smaller than in the situation of dense packing, but the relative size of the different ions in each structure is correct.

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 atoms (i.e. spheres) is the hexagonal structure shown on the left-hand side of Figure 1.6. To build a three-dimensional close-packed structure, one adds a second layer as in the middle of Figure 1.6. Now there are two possibilities, however, for adding a third layer. We can either put the atoms in the "holes" just on top of the first-layer atoms, or we can put them into the other type of "holes." The result are two different crystal structures. The first has an ABABAB… layer stacking sequence, the second an ABCABCABC… layer stacking sequence. Both have exactly the same packing density with the spheres filling about 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 1.16b. The fcc and hcp structures are very common in elemental metals, 36 chemical elements crystallizing in hcp and 24 in fcc lattices. 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 lattices, the coordination number is 12.

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



It is as yet an unresolved question why not all metals crystallize in the fcc or hcp structures, if coordination is indeed so important. Whereas a prediction of the actual structure for a given element is not possible on the basis of simple arguments, we can identify some factors that play a role. For example, structures that are not optimally packed, such as the bcc structure, have a lower coordination number, but they bring the second-nearest neighbors much closer to a given atom than in the close-packed structures. Another important consideration is that the bonding situation is often not quite so simple, particularly in **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 results in a much more directional character so that not only the close packing of the atoms is important.

The structures of many ionic solids can also be viewed as "close-packed" in some sense. One can derive 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 valence electrons of the atoms are not completely delocalized but shared between neighboring atoms, and bond lengths and directions 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 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 through a network of sp^2 hybrid bonds enclosing angles of 120°. The parent material of graphene is graphite, which consists of 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.

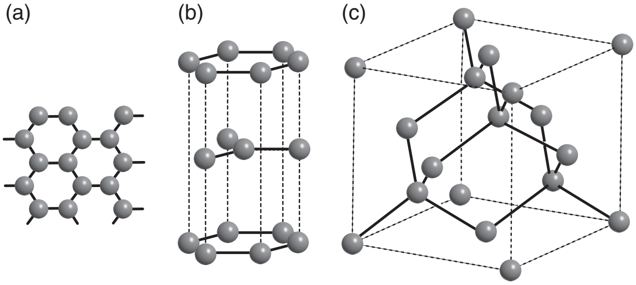


Figure 1.7 Structures for (a) graphene, (b) graphite, and (c) diamond. Bonds from sp^2 and sp^3 orbitals are displayed as solid lines.

The diamond structure is also found for Si and Ge. Many other isoelectronic materials (i.e. materials with the same total number of valence electrons), such as SiC, GaAs, or 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 this is X-ray diffraction. In fact, the importance of this technique extends far beyond solid state physics, as it has become an essential tool for fields such as structural biology as well. In biology, the idea is that you can derive the structure of a given protein by trying to crystallize it and then use the powerful methodology of X-ray diffraction to determine its structure. In addition, we will also use X-ray diffraction as a motivation to extend our formal description of structures.

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, meaning that we limit our analysis to the case that X-rays incident upon a crystal sample 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 in this book. Furthermore, we will assume that the X-ray source and detector are placed 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 will serve as a starting point for our analysis.

1.3.1.1 Bragg Theory

Bragg treated the problem as the reflection of the incident X-rays at flat crystal planes. These planes could, for example, be the close-packed planes making up fcc and hcp crystals, or they could be alternating Cs and Cl planes making up the CsCl structure. At first glance, the physical justification for this picture seems somewhat dubious, because the crystal planes appear certainly not “flat” for X-rays with wavelengths on the order of atomic spacing. Nevertheless, the description proved highly successful, and we 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 angles of incidence and emission are $90° - \Theta$. The condition for constructive interference is that the path length difference between the X-rays reflected from one layer and the next layer is

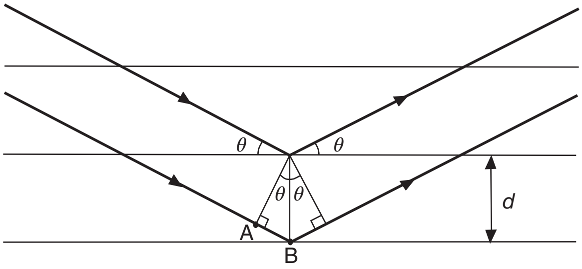


Figure 1.8 Construction for the derivation of the Bragg condition. The horizontal lines represent the crystal lattice planes that are separated by a distance *d*. The heavy lines represent the X-rays.

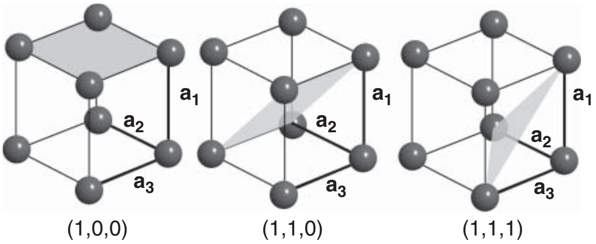
an integer multiple of the wavelength λ. In the figure, this means that $2AB = n\lambda$, where AB is the distance between points A and B and n is a natural number. On the other hand, we have $\sin\theta = AB/d$, which leads us to the **Bragg condition**

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

It is obvious that if this condition is fulfilled for one specific layer and the layer below it, then 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 in 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

Obviously, the Bragg condition will be satisfied 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. Thus, we need a more precise definition of the term **lattice plane**. It proves useful to define a lattice plane as a plane containing at least three non-collinear lattice points of a given Bravais lattice. If it contains three points, it will actually contain infinitely many because of the translational symmetry of the lattice. Examples for lattice planes in a simple cubic structure are shown in Figure 1.9.



(1,0,0) (1,1,0) (1,1,1)

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

Following this definition, all lattice planes can be characterized by a set of three integers, the so-called **Miller indices**. We derive them in three steps:

1) We find the intercepts of the specific plane at hand with the crystallographic axes in units of the lattice vectors, for example, $(1, \infty, \infty)$ for the leftmost plane in Figure 1.9.
2) We take the "reciprocal value" of these three numbers. For our example, this gives (1,0, 0).
3) We multiply the numbers obtained in this manner with some factor so that we arrive at the smallest set of integers having the same ratio. In the example given, this is not necessary as all number are already integers.

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 so that the incoming and reflected X-rays lie in a plane normal to a certain crystal plane. An elegant way to circumvent this problem is to use a powder consisting of very small crystals instead of a large single crystal. This will not only ensure that some of the many crystals are oriented correctly to get constructive interference from a certain set of crystal planes, it will also automatically yield 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 provide any information on what the lattice actually consists of, that is, the basis. Also, the fact that the X-rays are described as being reflected by planes is physically somewhat obscure. In the following, we will therefore 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

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

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