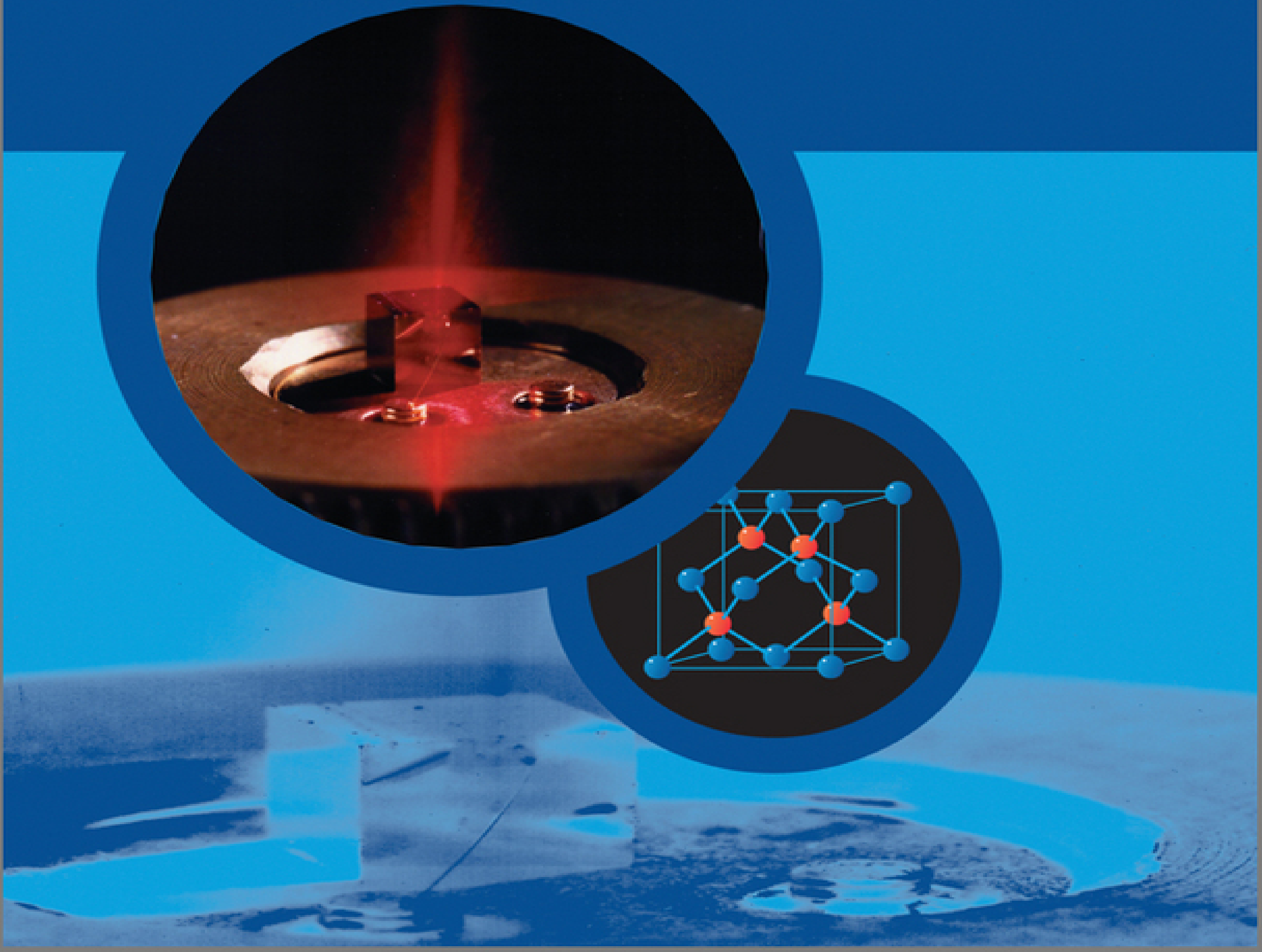
Solid State Physics

SECOND EDITION

J. R. Hook & H. E. Hall



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SOLID STATE PHYSICS

Second Edition

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To my family in partial compensation for taking so much of
my time away from them

Editors’ preface to the Manchester Physics Series

The Manchester Physics Series is a series of textbooks at first degree level. It grew out of our experience at the Department of Physics and Astronomy at Manchester University, widely shared elsewhere, that many textbooks contain much more material than can be accommodated in a typical undergraduate course; and that this material is only rarely so arranged as to allow the definition of a shorter self-contained course. In planning these books we have had two objectives. One was to produce short books: so that lecturers should find them attractive for undergraduate courses; so that students should not be frightened off by their encyclopaedic size or their price. To achieve this, we have been very selective in the choice of topics, with the emphasis on the basic physics together with some instructive, stimulating and useful applications. Our second objective was to produce books which allow courses of different lengths and difficulty to be selected, with emphasis on different applications. To achieve such flexibility we have encouraged authors to use flow diagrams showing the logical connections between different chapters and to put some topics in starred sections. These cover more advanced and alternative material which is not required for the understanding of latter parts of each volume.

Although these books were conceived as a series, each of them is self-contained and can be used independently of the others. Several of them are suitable for wider use in other sciences. Each Author's Preface gives details about the level, prerequisites, etc., of his volume.

The Manchester Physics Series has been very successful with total sales of more than a quarter of a million copies.

We are extremely grateful to the many students and colleagues, at Manchester and elsewhere, for helpful criticisms and stimulating comments. Our particular thanks go to the authors for all the work they have done, for the many new ideas they have contributed, and for discussing patiently, and often accepting, the suggestions of the editors.

Finally, we would like to thank our publishers, John Wiley & Sons Ltd, for their enthusiastic and continued commitment to the Manchester Physics Series.

D. J. Sandiford
F. Mandl
A. C. Phillips
February 1997

Foreword

> The story of the creation was told in 200 words. Look it up if you don't believe me.—*Edgar Wallace*

When the time came to consider a second edition of *Solid State Physics* I felt that I had already said what I had to say on the subject in the first edition. I also felt that the book was rather too idiosyncratic for many students. For these reasons I thought it would be better if the revision and updating were undertaken by another hand, and the editors shared this view.

We therefore approached Dr John Hook, a friend and colleague for many years, and I think the result justifies the decision. The new edition is, in my opinion, a substantial improvement on the old one, but it would not have occurred to me to write it like that.

September 1990

Henry Hall

Author’s preface to second edition

I accepted the invitation of the editors of the Manchester Physics Series to write a second edition of *Solid State Physics* for two main reasons. Firstly I felt that, although the approach adopted in the first edition had much to commend it, some re-ordering and simplification of the material was required to make the book more accessible to undergraduate students. Secondly there was a need to take account of some of the important developments that have occurred in solid state physics since 1973.

To achieve re-ordering and simplification it has been necessary to rewrite most of the first edition. A major change has been to introduce the idea of mobile electron states in solids through the free electron theory of metals rather than through the formation of energy bands by overlap of atomic states on neighbouring atoms. The latter approach was used in the first edition because it could be applied first to the dilute electron gas in semiconductors where an independent particle model might be expected to work. Although this was appealing to the experienced physicist, it proved difficult to the undergraduate student, who was forced to assimilate too many new ideas at the beginning. One feature of the first edition that I have retained is to delay for as long as possible a *formal* discussion of the reciprocal lattice and Brillouin zones in a three-dimensional crystal. Although these concepts provide an elegant general framework for describing many of the properties of crystalline solids, they are, like Maxwell’s equations in electromagnetism, more likely to be appreciated by students if they have met some of the ideas earlier in a simpler context. The use of the formal framework is avoided in the early chapters by using one- and two-dimensional geometries whenever necessary.

To take account of recent developments the amount of material on semiconductor physics and devices has been substantially increased, a chapter has been added on the two-dimensional electron gas and quantum Hall effect, and sections on quasi-crystals, high-T_C superconductors and the use of electrons to probe surfaces have been included. A chapter on the electrical properties of insulators has also been added.

I have tried to conform to the aim of the Manchester Physics Series by producing a book of reasonable length (and thus cost), from which it is possible to define self-contained undergraduate courses of different length and difficulty. The problem with solid state physics in this context is that it contains many diverse topics so that many quite different courses are possible. I have had to be very selective therefore in my choice of subjects, which has been strongly influenced by the third year undergraduate solid state physics courses at Manchester. We currently have a basic course of 20 lectures, which is given at two levels; the courses cover material from Chapters 1–5 of this book and the higher level course also incorporates appropriate sections of Chapters 11–13. A further course of 20 lectures on selected topics in solid state physics currently covers magnetism, superconductivity and ferroelectricity (Chapters 7–10). The flow diagram inside the front cover can be used as an aid to the design of courses based on this book.

Important subjects that are not covered in this book are crystal defects and disordered solids. I would have liked to include a chapter on each of these topics but would have exceeded the length limit set by the publishers and editors had I done so.

Like the first edition, this book presupposes a background knowledge of properties of matter (interatomc potentials and their relation to binding energies and elastic moduli, kinetic theory), quantum mechanics (Schrodinger's equation and its solution to find energy eigenvalues and eigenfunctions), electricity and magnetism (Maxwell’s equations and some familiarity with electric and magnetic fields in matter) and thermal physics (the Boltzmann factor and the Fermi and Bose distributions). Books in which this background information can be found are listed in the bibliography along with selected general reference books on solid state physics and some books and articles that provide further information on specific topics.

This book includes some more advanced and detailed material, which can be omitted without loss of continuity. Complete sections in this category are identified by starring and parts of sections are printed on a grey background.

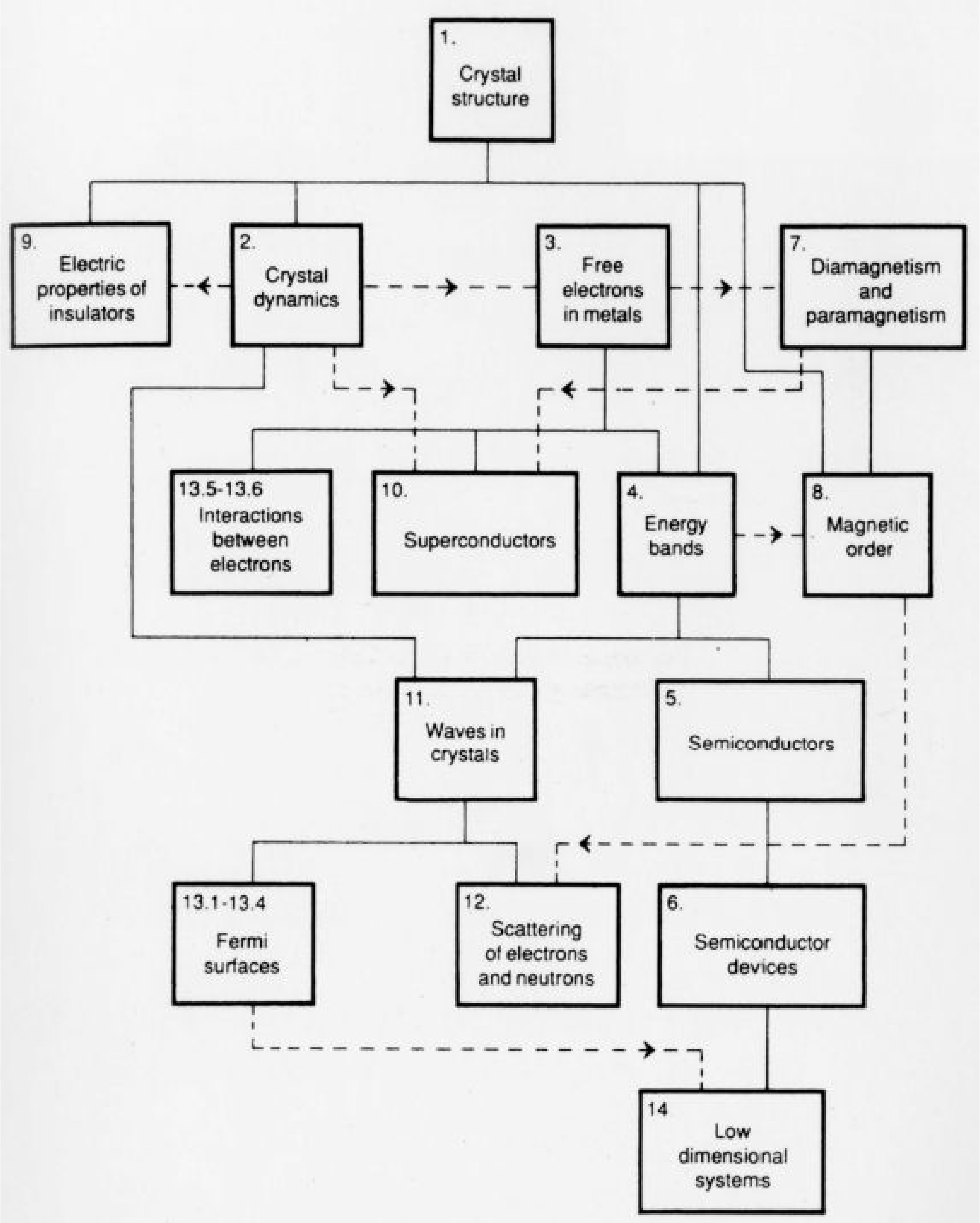
The use of **bold** type for a technical term in the text, normally when the term is first encountered, indicates that a definition or explanation of the term can be found there. *Italic* type is used for emphasis.

I am very grateful to David Sandiford and Henry Hall for their helpful advice and constructive criticism. I would also like to thank Manchester undergraduate Colin Lally, who read the manuscript from the point of view of a prospective consumer; his reaction reassured me that the level was appropriate. Ian Callaghan’s draughtmanship and photography was invaluable in producing many of the figures, and my son James helped willingly with some of the more mundane manuscript-preparation tasks.

September 1990

JOHN HOOK

FLOW DIAGRAM



Solid lines indicate essential prerequisites.
Dashed arrows indicate some assumption of material from a previous chapter.

Cover photography Visible light from a semiconductor laser developed at Philips Opteoelectronic in Eindhoven. (Photography provided by Professor Eoin O'Reilly of Surrey University and reproduced with the kind permission of Philips.)

CHAPTER 1

Crystal structure

Beauty when uncloth’d is clothèd best.—*Phineas Fletcher (1582–1650)*

1.1 INTRODUCTION

The aim of solid state physics is to explain the properties of solid materials as found on Earth. For almost all purposes the properties are expected to follow from Schrödinger’s equation for a collection of atomic nuclei and electrons interacting with electrostatic forces. The fundamental laws governing the behaviour of solids are therefore known and well tested. It is nowadays only in cosmology, astrophysics and high-energy physics that the fundamental laws are still in doubt.

In this book we shall be concerned almost entirely with crystalline solids, that is solids with an atomic structure based on a regular repeated pattern, a sort of three-dimensional wallpaper. Many important solids are crystalline in this sense, although this is not always manifest in the external form of the material. Because calculations are easier, more progress has been made in understanding the behaviour of crystalline than of non-crystalline materials. Many common solids—for example, glass, plastics, wood, bone—are not so highly ordered on an atomic scale and are therefore non-crystalline. Only recently has progress been made in understanding the behaviour of non-crystalline solids at a fundamental level.[†]

Even in the restricted field of crystalline solids the most remarkable thing is the great variety of *qualitatively different* behaviour that occurs. We have insulators, semiconductors, metals and superconductors—all obeying different macroscopic laws: an electric field causes an electric dipole moment in an insulator (Chapter 9), a steady current in a metal or semiconductor (Chapters 3 to 6) and a steadily accelerated current in a superconductor (Chapter 10). Solids may be transparent or opaque, hard or soft, brittle or ductile, magnetic or nonmagnetic.

In this chapter we first introduce in Section 1.2 the basic ideas of crystallography. In Section 1.3 we describe some important crystal structures and in Section 1.4 we explain how x-ray diffraction is used to determine crystal structure. In Section 1.5 we discuss quasi-crystals, ordered solids that challenge much of the conventional wisdom concerning crystalline materials. Section 1.6 contains a qualitative description of the interatomic forces responsible for binding atoms into solids.

1.2 ELEMENTARY CRYSTALLOGRAPHY

A basic knowledge of crystallography is essential for solid state physicists. They must know how to specify completely, concisely and unambiguously any crystal structure and they must be aware of the way that structures can be classified into different types according to the symmetries they possess; we shall see that the symmetry of a crystal can have a profound influence on its properties. Fortunately we will be concerned in this book only with solids with simple structures and we can therefore avoid the sophisticated group theoretical methods required to discuss crystal structures in general.

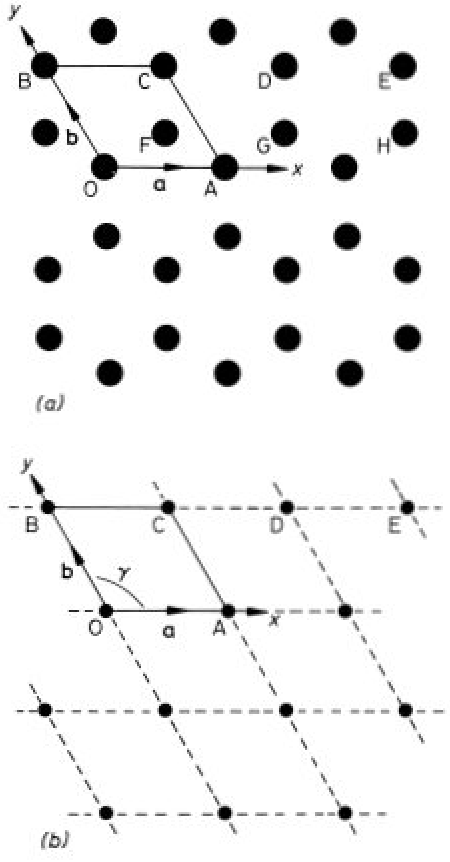
1.2.1 The crystal lattice

We will use a simple example to illustrate the methods and nomenclature used by crystallographers to describe the structure of crystals. Graphite is a crystalline form of carbon in which hexagonal arrays of atoms are situated on a series of equally spaced parallel planes. The arrangement of the atoms on one such plane is shown in Fig. 1.1(*a*). We choose graphite for our example because a single two-dimensional plane of atoms in this structure illustrates most of the concepts that we need to explain. Solid state physicists often resort to the device of considering a system of one or two dimensions when confronted with a new problem; the physics is often (but not *always*) the same as in three dimensions but the mathematics and understanding can be much easier.

To describe the structure of the two-dimensional graphite crystal it is necessary to establish a set of coordinate axes within the crystal. The origin can in principle be anywhere but it is usual to site it upon one of the atoms. Suppose we choose the atom labelled O in Fig. 1.1(*a*) for the origin. The next step is a very important one; we must proceed to identify all the positions within the crystal that are identical in all respects to the origin. To be identical it is necessary that an observer situated at the position should have exactly the same view in any direction as an observer situated at the origin. Clearly for this to be possible we must imagine that the two-dimensional crystal is infinite in extent. Readers should convince themselves that the atoms at A, B, C, D and E (and eight others in the diagram) are identical to the atom at the origin but that the atoms at F, G and H are not; compare for example the directions of the three nearest neighbours of the atom at O with the directions of the three nearest neighbours of the atom at F. The set of identical points identified in this way is shown in Fig. 1.1(*b*) and is called the **crystal lattice**; comparison of

Figs. 1.1(*a*) and (*b*) illustrates clearly that the lattice is not in general the same as the structure. Readers should convince themselves that, apart from an unimportant shift in position, the lattice is independent of the choice of origin. Having identified the crystal lattice in this way the coordinate axes are simply obtained by joining the lattice point at the origin to two of its neighbours.

Fig. 1.1 Two-dimensional crystal of carbon atoms in graphite: (*a*) shows how the atoms are situated at the corners of regular hexagons; (*b*) shows the crystal lattice obtained by identifying all the atoms in (*a*) that are in identical positions to that at O. The crystal axes, lattice vectors and conventional unit cell are shown in both figures



There are many ways of doing this but the **conventional** choice for graphite is to take OA and OB for the *x* and *y* axes as shown in Fig. 1.1(*b*). Note that the coordinate axes for graphite are not orthogonal. An example of an unconventional choice of coordinate axes for graphite would be to take OA for the x axis as before but to take the OD direction for the y axis. The distances and directions of the nearest lattice points along the x and y axes are specified by the **lattice vectors a** and **b** respectively (Fig. 1.1.(*b*)). The crystal lattice is completely defined by giving the lengths of **a** and **b** and the angle γ between them. For graphite we have $a = b = 2.46$ Å, $\gamma = 120°$ (1 Å = 1 ångstrom = 10^{-10} m). The conventional choice of axes for graphite therefore clearly reflects the hexagonal symmetry of the structure; this is not the case for the unconventional choice discussed above.

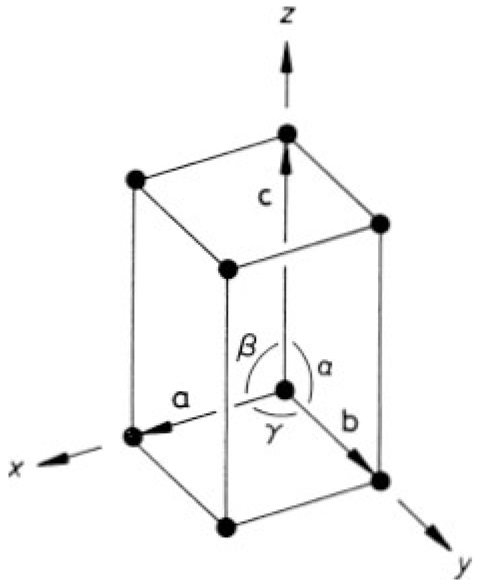
The positions of all the lattice points of the two-dimensional graphite crystal are reached by drawing all possible vectors of the form

$$\text{(1.1)} \quad \mathbf{r} = u\mathbf{a} + v\mathbf{b}$$

from the origin, where u and v take on all possible integer values, positive, negative and zero. That the crystal appears identical when viewed from all the positions given by this equation is an indication that it possesses the important property of **translational invariance**.

The generalization of the above ideas to a three-dimensional crystal is straightforward. An origin is chosen and all the points within the crystal that are identical to it are identified; this set of points constitutes the three-dimensional crystal lattice. The directions of the crystal coordinate axes are then defined by joining the lattice point at the origin to *three* of its near neighbours (Fig. 1.2). The choice of neighbours is sometimes obvious but, where this is not the case, convention usually dictates the choice that most clearly reflects the symmetry of the lattice. The distances and directions of the nearest lattice points along the crystallographic x, y and z axes are specified by the *three* lattice vectors **a**, **b** and **c**. The lattice is completely specified by giving the lengths of **a**, **b** and **c**, and the angles α, β, and γ between them (Fig. 1.2). The positions of all the lattice points are reached by drawing all possible vectors of the form

Fig. 1.2 Crystallographic axes and unit cell for a three-dimensional crystal lattice



$$\mathbf{r} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c} \qquad (u,\ v \text{ and } w \text{ are integers}) \tag{1.2}$$

from the origin. The ability to express the positions of the points in this way, with a suitable choice of **a**, **b** and **c**, may be taken as a definition of a lattice in crystallography. A crystalline material may be defined as a material that possesses a lattice of this kind; the translational invariance property of the crystal is that it appears identical from all positions of the form of Eq. (1.2). Note that the only effect of a shift in choice of origin on a crystal lattice is a shift in the lattice as a whole by the same amount.

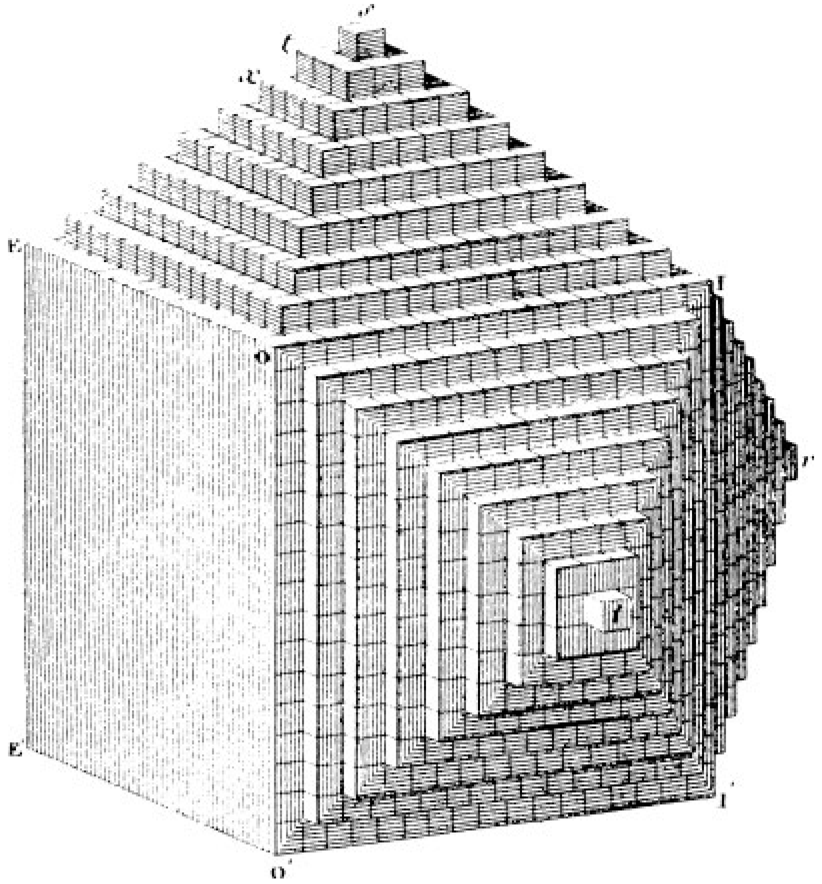
The lattice vectors also define the **unit cell** of a crystal. This concept is most easily explained by returning to the two-dimensional graphite crystal of Fig. 1.1, for which the unit cell is the parallelogram OACB defined by the vectors **a** and **b**. It is so called because stacking such cells together generates the entire crystal lattice, as is indicated by the broken lines in Fig. 1.1(*b*). The analogous three-dimensional object in Fig. 1.2, defined by lattice vectors **a**, **b** and **c**, is called a parallelopiped and is the unit cell for the three-dimensional lattice. The unit cell obtained from the conventional choice of lattice vectors is known as the **conventional unit cell**.

The concept of the unit cell as a building block allows us to understand the remarkable similarities between different crystals of the same material. In particular we can explain the law of constancy of angle (first stated by Nicolaus Steno in 1761) that: *In all crystals of the same substance the angles between corresponding faces have a constant value*. Fig. 1.3 is an illustration from an early book on mineralogy showing how macroscopically plane faces in various orientations can be built up by using cubic unit cells as building blocks. We shall see in Chapter 12 that the surfaces of crystals are *not* in fact constructed in the manner suggested by this illustration.

The reader will have noticed that the two-dimensional lattice of graphite (Fig. 1.1(*b*)) possesses symmetry properties other than the translational invariance indicated by Eq. (1.1). The lattice is transformed into itself, for example, by a rotation of 60° about an axis perpendicular to the *xy* plane through a lattice point; this axis is the crystallographic *z* axis of graphite, which is therefore a sixfold rotation axis of the *lattice*. In 1845 Bravais deduced that any three-dimensional lattice of the form of Eq. (1.2) could be classified into one of 14 possible types according to the symmetry that it possessed. The 14 **Bravais lattices** contain only one-, two-, three-, four- and six-fold rotation axes.

We will not describe all 14 Bravais lattices since only a few will feature in this book, but to illustrate the principle of the classification of lattices by symmetry we consider the corresponding two-dimensional problem. A two-dimensional lattice is specified by *a*, *b* and the angle *γ* between **a** and **b**. A lattice with translational symmetry only is shown in Fig. 1.4(*a*) with three possible choices of primitive unit cell. Lattices of higher symmetry are shown in Figs. 1.4(*b*)-(*e*). The **rectangular lattice** in Fig. 1.4(*b*) has *γ* = 90°. Alternatively with a general value of *γ* we may have *a* = *b*, giving the **rhombic lattice** shown in Fig. 1.4(*c*). This latter example is interesting in that it shares some symmetries with the rectangular lattice and it can also be described by the rectangular unit cell defined by **a**′ and **b**′. This rectangular unit cell has a lattice point at the centre as well as at the corners and the rhombic lattice may therefore also be referred to as a **centred rectangular lattice**. The unit cell defined by **a**′ and **b**′ has an area twice that defined by **a** and **b**. The latter is the smallest possible unit cell of the lattice and is said therefore to be a **primitive unit cell**; the former unit cell is consequently a **non-primitive unit cell**. We will encounter examples of both primitive and non-primitive three-dimensional unit cells in Section 1.3. To complete our survey of two-dimensional lattices we must consider the possibility *a* = *b* combined with a special value of *γ*. Two cases arise: *γ* = 60° (or 120°) gives the **triangular lattice** of Fig. 1.4(*d*) with each lattice point surrounded by six neighbours at the corners of a regular hexagon; and *γ* = 90° gives the **square lattice** of Fig. 1.4(*e*). The two-dimensional graphite lattice of Fig. 1.1(*b*) is a triangular lattice.

Fig. 1.3 The way in which the stacking of cubic unit cells can produce crystal faces of different orientations (Hauy, *Traite de crystallographie*)



[Fig. 1.4](#) The five possible types of crystal lattice in two dimensions, (*a*) Lattice with translational symmetry only, showing three possible primitive unit cells, (*b*) Rectangular lattice, $\gamma = 90°$. (*c*) Rhombic lattice, $a = b$, equivalent to a centred rectangular lattice with the non-primitive unit cell defined by **a**′ and **b**′. (*d*) Triangular lattice, $a = b$, $\gamma = 60°$. (*e*) Square lattice, $a = b$, $\gamma = 90°$