PRINCIPLES OF THE THEORY OF SOLIDS

BY

J. M. ZIMAN, F.R.S.

SECOND EDITION

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PREFACE

The Frontiers of Knowledge (to coin a phrase) are always on the move. Today's discovery will tomorrow be part of the mental furniture of every research worker. By the end of next week it will be in every course of graduate lectures. Within the month there will be a clamour to have it in the undergraduate curriculum. Next year, I do believe, it will seem so commonplace that it may be assumed to be known by every schoolboy.

The process of advancing the line of settlements, and cultivating and civilizing the new territory, takes place in stages. The original papers are published, to the delight of their authors, and to the critical eyes of their readers. Review articles then provide crude sketch plans, elementary guides through the forests of the literature. Then come the monographs, exact surveys, mapping out the ground that has been won, adjusting claims for priority, putting each fact or theory into its place.

Finally we need textbooks. There is a profound distinction between a treatise and a textbook. A treatise expounds; a textbook explains. It has never been supposed that a student could get into his head the whole of physics, nor even the whole of any branch of physics. He does not need to remember what he can easily discover by reference to monographs, review articles and original papers. But he must learn to *read* those references: he must learn the language in which they are written: he must know the basic experimental facts, and general theoretical principles, upon which his science is founded.

This book aims to present, as simply as possible, the elements of the theory of the physics of perfect crystalline solids. It is a book full of *ideas*, not facts. It is an exposition of the principles, not a description of the phenomena.

A theory is an analysis of the properties of a hypothetical model. In physics, which may almost be defined as the intellectual exercise of subsuming the universe to mathematics, our models are mathematical. The theories discussed in this book are mathematical theories; the most important concepts in the field, such as 'the Fermi Surface', are abstract mathematical constructions, which cannot be explained or understood properly without formal analysis.

What I have tried to do is to give a self-contained mathematical treatment of the simplest model that will demonstrate each principle. If most of the interesting properties of superconductors can be derived from a model of free electrons with a curtailed attractive interaction, then that is the framework of the calculation. At this stage, it is better to appreciate the conditions that are essential to the appearance of the phenomenon at all, than it is to try to wield far heavier equations, based upon more realistic but much more complex physical specifications, in order to anticipate the observed deviations from the simple formulae. The reader must go to the original papers and treatises for these elaborations of the elementary models.

On the other hand, having defined the model, one must not shirk the mathematical analysis. It is my experience that the direct derivation of many simple, well-known formulae from first principles is not easy to find in print. The original papers do not follow the easiest path, the authors of reviews find the necessary exposition too difficult—or beneath their dignity—and the treatises are too self-conscious about completeness and rigour. I have tried to make the mathematical argument complete in itself—or at least intelligible in principle—without frequent appeal to that *deus ex machina* of the tired author 'it can be shown that...'. An advantage of trying to cover such a wide field is that one can invoke general principles, such as Bloch's theorem and the theory of zones, to unify many branches of the subject and save much mental effort.

How much is the reader expected to know already? He should be acquainted with the elementary descriptive facts about solids—for example, the free-electron theory of metals—as taught in undergraduate courses. I also assume the elements of quantum mechanics—especially the Schrödinger equation, perturbation theory, and the theory of scattering—such as graduate students of experimental physics are now expected to acquire. I have tried to keep the mathematical techniques to that level; whenever the algebra threatened to get difficult, I have stopped. There are no density matrices, bubble diagrams, branch points, character tables, or other bits and pieces of the apparatus of advanced theory; professional 'theoreticians' must look elsewhere for their fodder.

For the benefit of those reviewers who judge a book by what is absent from it, let me admit that there is no serious discussion of alloys, dislocations, F-centres, impurity centres, etc. There is nothing about magnetic resonances associated with single atoms or nuclei, and no attempt to interpret essentially macroscopic phenomena such as ferromagnetic domains, p–n junctions or the intermediate state of a superconductor. The exclusion of all except simple, perfect, crystalline solids is artificial, but it is convenient, for it gives some unity to the discourse, which is centred on the mathematical consequences of lattice periodicity. Also, friends, life is short.

No novelty is claimed for this account of an active branch of physics. These are the theories that are currently used, and accepted as well established, by those who work in this field. There is no attempt to criticize the theories, to discuss their validity as interpretations of natural phenomena, to derive them with full mathematical rigour, or to demonstrate the full flowering of their applications. The effort has been focused upon clarity of exposition. The reader is being asked to grasp new concepts; let him suspend his critical faculties until he has understood what the new ideas mean; if, then, he is rightly sceptical, let him turn to the enormous literature upon which this science is built, and help his unbelief from those copious, if muddy, sources. I have deliberately refrained from making any direct reference to the original papers; for such information the student should consult the monographs and review articles listed at the end of the book.

This book began as a course of lectures for graduate students of Theoretical and Experimental Physics in the University of Cambridge: it was written in my last two terms, and completed in my last few weeks, of active membership of the staff of the Cavendish Laboratory. It is a great privilege to have belonged, for nine years, to that peerless institution. I am only too conscious of the impossibility of living up to the unique standard that it has set, and continues to set, in the world of physics.

But the Cavendish is more than a famous laboratory; it is an abode of humanity and friendship. May I offer thanks to those friends—especially to Nevill Mott, to Brian Pippard, and to Volker Heine—who brought me to Cambridge, who welcomed me, taught me, wisely controverted me, abundantly assisted me, and generally made life here agreeable, interesting and exciting. They have heard the music of the spheres; and yet they know that science is made for man, not man for science.

J. M. Z.

Cavendish Laboratory, Cambridge
June 1963

PREFACE TO THE SECOND EDITION

This new edition is meant still to conform to the principles expounded in the above Preface. But eight years is about the doubling time of modern scientific knowledge and solid state physicists have not been idle in the interval. Most of the original text still stands, but several new sections have been added, to cover topics that have come into greater prominence lately or where there has been a significant shift of understanding or emphasis. I have also attempted to make reference in passing to a number of phenomena or fields of study that are relevant to the basic theory, even if they cannot be discussed in detail. In this way, the general scope of the book has been widened, to include, for example, something about magnetic and non-magnetic impurities, *F*-centres, surfaces, tunnelling, junctions, and type II superconductivity. But the general level of mathematical sophistication has not been raised, even though the technical formalism of advanced quantum theory is now becoming more commonplace in this field.

I am most grateful to many colleagues—especially to Bob Chambers here in Bristol and to Federico Garcia-Moliner in Madrid—for a number of detailed comments of which I have tried to take account in the new text. Bob Evans helped greatly by preparing a new index. And lest the reader may feel that absence from Cambridge has been a long period of exile, may I simply add that Bristol, too, is just as good a 'ole to go to.

J. M. Z.

H. H. Wills Physics Laboratory, Bristol
March 1971

CONTENTS

CHAPTER 1

PERIODIC STRUCTURES

Again! again! again! THOMAS CAMPBELL

1.1 Translational symmetry

A theory of the physical properties of solids would be practically impossible if the most stable structure for most solids were not a regular crystal lattice. The N-body problem is reduced to manageable proportions by the existence of *translational symmetry*. This means that *there exist basic vectors*, $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ *such that the atomic structure remains invariant under translation through any vector which is the sum of integral multiples of these vectors.*

In practice, this is only an ideal. A laboratory specimen is necessarily finite in size, so that we must not carry our structure through the boundary. But the only regions where this matters are the layers of atoms near the surface, and in a block of N atoms these constitute only about $N^{2/3}$ atoms—say 1 atom in 10^8 in a macroscopic specimen. Most crystalline solids are also structurally imperfect, with defects, impurities and dislocations to disturb the regularity of arrangement of the atoms. Such imperfections give rise to many interesting physical phenomena, but we shall ignore them, except incidentally, in the present discussion. We are mainly concerned here with the perfect ideal solid, and with the properties it shows; the phenomena which are associated with the solid as the matrix, vehicle, or background for little bits of dirt, or tiny cracks and structural flaws, belong to a different realm of discourse.

We represent the translational group by a *space lattice* or *Bravais net*. Start from some point and then construct all points reached from it by the basic translations. These are the *lattice sites*, defined by the set

$$\mathbf{l} = l_1\mathbf{a}_1 + l_2\mathbf{a}_2 + l_3\mathbf{a}_3, \tag{1.1}$$

where l_1, l_2, l_3 are integers (Fig. 1).

But a solid is a physical structure—not a set of mathematical points. Suppose that there are some atoms, etc., in the neighbourhood of our origin O. The translational invariance insists that there must be exactly similar atoms, placed similarly, about each lattice site (*Fig. 2*).

It is obvious that we can define the physical arrangement of the whole crystal if we specify the contents of a single *unit cell*—for example, the parallelepiped subtended by the basic vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$. The whole crystal is made up of endless repetitions of this object stacked like bricks in a wall. But the actual definition of a unit cell is to some extent arbitrary. It is obvious enough that any parallelepiped of the right size, shape and orientation would do—as we see in

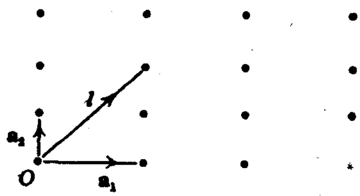


Fig. 1

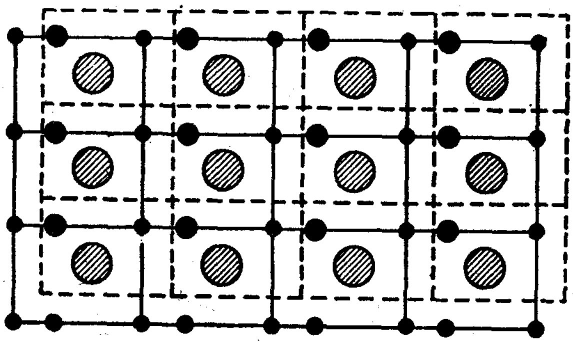


Fig. 2. Alternative unit cells.

Fig. 2. What is, perhaps, not quite so obvious is that the shape can be altered to some extent. Suppose, for example, that there is some central symmetry about some point in the structure (and hence, about all equivalent points). This would be a convenient point to choose as the centre of a cell, itself with central symmetry. One can do this systematically by constructing a *Wigner–Seitz* cell, that is, by drawing the perpendicular bisector planes of the translation vectors from the chosen centre to the nearest equivalent lattice sites. The volume inside all the bisector planes is obviously a unit cell—it is the region whose elements lie nearer to the chosen centre than to any other lattice site.

The unit cell can contain one or more atoms. Naturally, if it contains only one atom, we centre that on the lattice site, and say that we have a *Bravais lattice*. If there are several atoms per unit cell, then we have a *lattice with a basis*. In most of what follows, we shall assume, without special notice, that the structure is a Bravais lattice. This is for simplicity; in reality only a few elementary solids, such as the alkali metals, have this structure.

The science of *crystallography* is concerned with the enumeration and classification of all possible types of crystal structure, and the determination of the actual structure of actual crystalline solids.

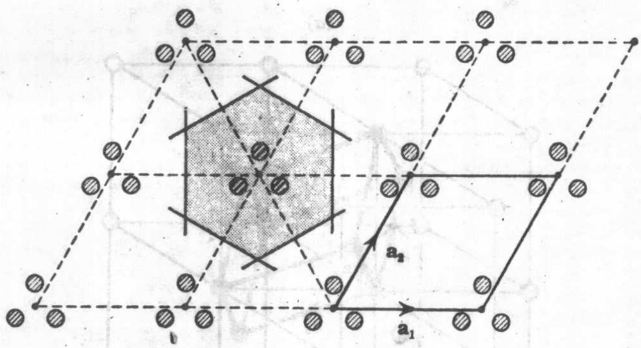
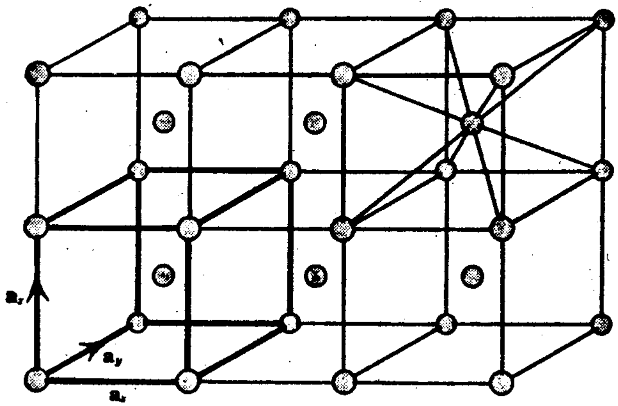


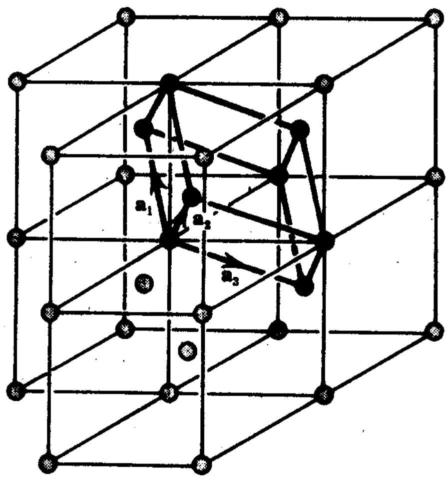
Fig. 3. Wigner–Seitz cell.

Structures are classified according to their symmetry properties, such as invariance under rotation about an axis, reflection in a plane, etc. These symmetries are often of great importance in the simplification of theoretical computations, and can be used with great power in the discussion of the numbers of parameters that are necessary to define the macroscopic properties of solids. However, to take full advantage of this theory, one needs the mathematics of *group theory*, which would take us too far away from our main topic. If we restrict ourselves mainly to very simple solids, then most of the symmetry properties can be discovered by inspection without formal algebraic analysis. In any case, there are many excellent books on crystallography and on group theory and its applications to the theory of solids.

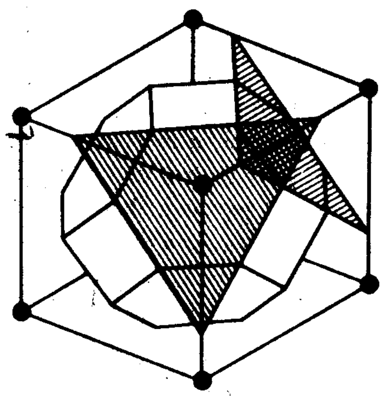
In these books, the various types of Bravais lattice, etc., are set out in detail. We shall consider here only one case, which exemplifies many of the principles of the subject, and which is also of great importance as a structure which is actually assumed by some elements. This is the *body-centred cubic* (B.C.C.) structure illustrated in Fig. 4.



(a)



(b)



(c)

Fig. 4. Body-centred cubic lattice. (*a*) Cubic unit cell. (*b*) Generators of the Bravais lattice. (*c*) Wigner–Seitz cell.

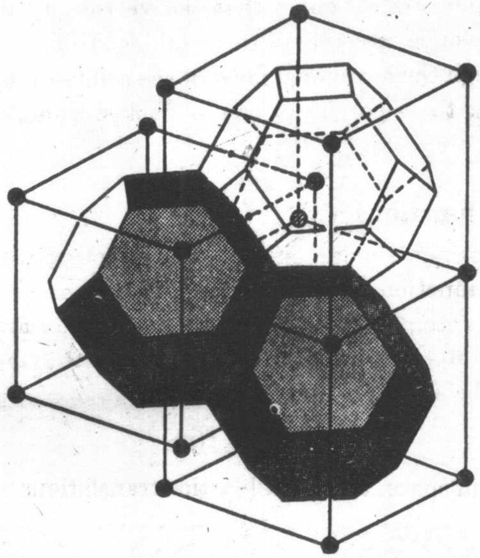


Fig. 5. Stacking Wigner–Seitz cells of the B.C.C. lattice.

At first sight, this is a cubic lattice with two atoms per unit cell, or two interpenetrating simple cubic sublattices defined by

$$\left.\begin{aligned} \boldsymbol{l} &= l_x \mathbf{a}_x + l_y \mathbf{a}_y + l_z \mathbf{a}_z, \\ \boldsymbol{l}' &= (l_x + \tfrac{1}{2})\,\mathbf{a}_x + (l_y + \tfrac{1}{2})\,\mathbf{a}_y + (l_z + \tfrac{1}{2})\,\mathbf{a}_z, \end{aligned}\right\} \qquad (1.2)$$

where l_x, l_y, l_z are all integers. But if we write

$$\left.\begin{aligned} \mathbf{a}_1 &= \tfrac{1}{2}(-\mathbf{a}_x + \mathbf{a}_y + \mathbf{a}_z), \\ \mathbf{a}_2 &= \tfrac{1}{2}(\mathbf{a}_x - \mathbf{a}_y + \mathbf{a}_z), \\ \mathbf{a}_3 &= \tfrac{1}{2}(\mathbf{a}_x + \mathbf{a}_y - \mathbf{a}_z), \end{aligned}\right\} \qquad (1.3)$$

we can generate all the points of both sublattices by

$$\boldsymbol{l} = l_1 \mathbf{a}_1 + l_2 \mathbf{a}_2 + l_3 \mathbf{a}_3 \qquad (1.4)$$

with l_1, l_2, l_3 integers. We shall find ourselves at a cube centre, or corner, according as $(l_1 + l_2 + l_3)$ is odd, or even.

Thus (Fig. 4(*b*)) this is really a Bravais lattice. Instead of using a cubic unit cell we may use the Wigner–Seitz cell (Fig. 4(*c*)), which is constructed by chopping off all the corners of a cube half way along a diagonal from the centre to a corner point. This figure obviously has the same symmetry as a cube—for example, the original vectors, $\mathbf{a}_x, \mathbf{a}_y, \mathbf{a}_z$ are axes of four-fold symmetry. It also shows, more clearly perhaps than the original cube, that the vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$, i.e. the diagonals of the cube, are axes of three-fold rotational symmetry, for they pass through the hexagonal faces of the cell. It is a good exercise to visualize how these polyhedra can be packed to make the original lattice (Fig. 5).

1.2 Periodic functions

To define a physical model of a crystal structure we need to give values to some function $f(\mathbf{r})$ in space—local electron density, electrostatic potential, etc., which can be recognized as an arrangement of atoms (e.g. Fig. 6). Our assertion of translational symmetry means that this must be a *multiply periodic function*

$$f(\mathbf{r}+\boldsymbol{l}) = f(\mathbf{r}) \tag{1.5}$$

for all points $\mathbf{r}$ in space, and for all lattice translations.

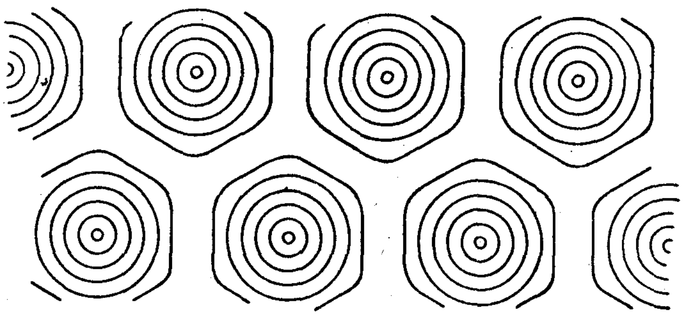


Fig. 6. Multiply periodic function.

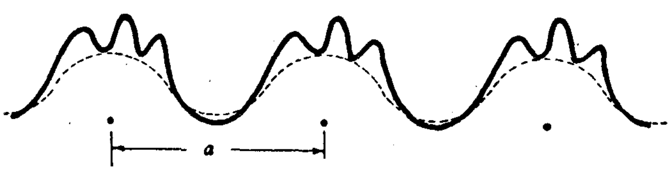


Fig. 7

In one dimension we are perfectly familiar with periodic functions. Thus, as in Fig. 7, we may have

$$f(x+l) = f(x), \tag{1.6}$$

where l is of the form $l_1 a$, with l_1 an integer and a the period of the function. We also know that any such function can be expressed as a *Fourier series*,

$$f(x) = \sum_n A_n e^{2\pi i n x/a}, \tag{1.7}$$