Solid State Physics

H. E. HALL

SOLID STATE PHYSICS

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The Manchester Physics Series

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Editors' Preface to the Manchester Physics Series

In devising physics syllabuses for undergraduate courses, the staff of Manchester University Physics Department have experienced great difficulty in finding suitable textbooks to recommend to students; many teachers at other universities apparently share this experience. Most books contain much more material than a student has time to assimilate and are so arranged that it is only rarely possible to select sections or chapters to define a self-contained, balanced syllabus. From this situation grew the idea of the Manchester Physics Series.

The books of the Manchester Physics Series correspond to our lecture courses with about fifty per cent additional material. To achieve this we have been very selective in the choice of topics to be included. The emphasis is on the basic physics together with some instructive, stimulating and useful applications. Since the treatment of particular topics varies greatly between different universities, we have tried to organize the material so that it is possible to select courses of different length and difficulty and to emphasize different applications. For this purpose we have encouraged authors to use flow diagrams showing the logical connection of different chapters and to put some topics into starred sections or subsections. These cover more advanced and alternative material, and are not required for the understanding of later parts of each volume.

Since the books of the Manchester Physics Series were planned as an integrated course, the series gives a balanced account of those parts of physics which it treats. The level of sophistication varies: '*Properties of Matter*' is for the first year, '*Solid State Physics*' for the third. The other volumes are intermediate, allowing considerable flexibility in use. '*Electromagnetism*', '*Optics*', '*Electronics*' and '*Atomic Physics*' start from first year level and progress to material suitable for second or even third year courses. '*Statistical Physics*' is suitable for second or third year. The books have been written in such a way that each volume is self-contained and can be used independently of the others.

Although the series has been written for undergraduates at an English university, it is equally suitable for American university courses beyond the Freshman year. Each author's preface gives detailed information about the prerequisite material for his volume.

In producing a series such as this, a policy decision must be made about units. After the widest possible consultations we decided, jointly with the authors and the publishers, to adopt SI units interpreted liberally, largely following the recommendations of the International Union of Pure and Applied Physics. We did not outlaw physical units such as the electron-volt. Nor were we pedantic about factors of 10 (is 0.012 kg preferable to 12 g?), about abbreviations (while s or sec may not be equally acceptable to a computer, they should be to a scientist), and about similarly trivial matters.

Preliminary editions of these books have been tried out at Manchester University and circulated widely to teachers at other universities, so that much feedback has been provided. We are extremely grateful to the many students and collegues, at Manchester and elsewhere, who through criticisms, suggestions and stimulating discussions helped to improve the presentation and approach of the final version of these books. 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 frequently accepting, our many suggestions and requests. We would also like to thank the publishers, John Wiley and Sons, who have been most helpful in every way, including the financing of the preliminary editions.

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Author's Preface

In keeping with the general aims of the Manchester Physics Series I have tried to write a short book containing all the solid state physics that an honours student, with some special interest in the subject, should learn—*but no more*. This book is therefore very far from comprehensive in its coverage; the amount of factual information presented has been pruned with extreme severity. The facts presented have been selected mainly on the criterion of usefulness in explaining basic principles, and I have tried to make these explanations clear and complete. I have simplified the arguments as far as possible, so that the essentials may be grasped; but, as befits the intellectual ability of honours students, I have not shirked the discussion of difficult ideas or dubious assumptions. I have particularly had in mind that students using this book will have to cope with physics thirty years hence, and have therefore largely avoided the description of currently fashionable calculation methods, but have emphasized basic assumptions. The central theme of this book is the large variety of *qualitatively different* ground states that an assembly of atoms can have; I hope I have said sufficient to warn the reader to watch out for surprises!

The general plan of the book is shown on the flow diagram inside the front cover. This plan has been determined largely by two factors:

(1) After several years teaching a course for honours physicists based firmly on reciprocal lattice and Brillouin zone theory, and an attempt to give a much simpler course to honours chemists, largely avoiding these topics, I have come to the conclusion that they are the 'Maxwell's equations' of solid

state physics. The reciprocal lattice and Brillouin zones are an elegant formal structure from which much of solid state theory can be deduced; but they are much better appreciated as a unifying principle after some simpler things have been done without their aid. For this reason the general discussion of waves in periodic structures in Chapter 6 is preceded by one-dimensional discussions of phonons in Chapter 2, electrons in Chapter 3, and magnons in Chapter 5.

(2) In the new course structure at Manchester the second half of the solid state course is optional; I therefore wanted the first half of the book to constitute a suitable introductory course, containing some important applications. It is for this reason that the whole treatment of semiconductors is in Chapter 3. It seemed logically preferable to reverse the usual order and treat semiconductors before metals, since the former are conceptually easier because the electron gas is dilute; also, the discussion of divalent metals requires the extension of energy bands to two dimensions, and should therefore come later.

Another feature worthy of comment is that I have put more chemistry and less crystallography than is usual in Chapter 1. The crystal structures one actually needs to know are few; the hydrogen molecule is not only fundamental to atomic binding, but is also an easy example with which to illustrate both the simplicity and the doubtful validity of the independent particle approximation—a point I wanted to make right from the start. The structure of Chapter 1 has been rather carefully organized so that, by the judicious use of optional starred sections and appendices, this key introductory chapter may be read at a wide range of levels, according to the tastes and abilities of the student.

I hope that these considerations have given the book a structure that will make it suitable for courses of honours degree standard that vary considerably in length, breadth, and depth. The chapters are of rather unequal length, but as a rough general guide I would recommend four or five 50-minute lectures per chapter as an adequate allowance; the whole book thus contains material for over fifty lectures, more than would usually be given in any undergraduate course. The flow diagram inside the front cover will enable a suitable selection to be made. Thus, a short introductory course at full breadth can be based on Chapters 1–5; but a narrower course of similar length directed specifically at the band structure of metals could be based on Chapters 1, 3, 4, 6, 9 and 10. As a further aid to selection, sections and subsections that may be omitted without loss of continuity are indicated by a star ★ at the left of the heading, and paragraphs in this category are printed on a grey background; these optional sections are often rather harder. Also, the appendices may be omitted if the student is prepared to take results on trust. It is thus by the omission or inclusion of starred section and appendices that the level at which this book is read may be most conveniently adjusted.

As used at Manchester this book presupposes courses based on Willmott's '*Atomic Physics*' and Mandl's '*Statistical Physics*',[2] but one could if necessary get away with considerably less preparation: for quantum mechanics, Heitler's '*Wave Mechanics*';[9] and for statistical mechanics, familiarity with the Boltzmann factor and acceptance of the Bose and Fermi distribution functions. In electromagnetism, Maxwell's equations are assumed known, and some idea of magnetic fields in matter on the lines of Vol. 2 of the Berkeley Physics Course.[4]

In accordance with editorial policy and current educational practice I have used SI units in this book as fully as seems reasonable. An important exception to standard SI practice occurs in electromagnetism where, to avoid confusion in discussing fields in matter, I have defined **H** so that it is measured, like **B**, in tesla, with other consequential changes. A full description of units in electromagnetism is given in Appendix E.

On the few occasions where formulae from atomic physics occur I have written them also in terms of the fine structure constant $\alpha = (e^2/4\pi\varepsilon_0 hc)$; this gives formulae that are not only more concise, but are also independent of the system of units. I have also departed from strict SI in not eschewing such useful units as the Angstrom, the electron volt, the Rydberg, and the Bohr radius.

I should perhaps conclude with an apology for writing this book at all. I look like a solid state physicist only when viewed from a coordinate system centred on the Physics Department at Manchester, which is dominated by nuclear physics and radioastronomy; because I am not a professional I have merely treated the topics that interest me in a way that I can understand. I have therefore probably used methods that cannot be developed into a more proper treatment, and I hope the professionals will forgive me; I also hope they will tell me, as kindly as possible, of the errors they find.

I would finally like to thank the many people who have helped me with comments on the preliminary edition. I am especially grateful to Drs. F. Mandl, P. G. J. Lucas, and D. J. Sandiford for their detailed and constructive criticism of successive versions of this book. I should also like to thank Dr. Lucas for allowing me to use some of his problems, and him and Drs. J. R. Hook and I. S. Mackenzie for checking the solutions. I am grateful to the copyright holders for permission to use many published figures, as specifically acknowledged in the text, and especially to the authors for providing original photographs for Figs. 1.28, 1.29, 10.12 and 12.5.

April 1973 H. E. HALL

[2,4,9] : References by number are to the bibliography.

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CHAPTER 

Crystal structure

1.1 INTRODUCTION

Solid state physics is concerned with attempting to account for the properties of ordinary matter as found on Earth. For almost all purposes the properties of such matter are expected to follow from Schrödinger's equation for a collection of permanent atomic nuclei and electrons interacting with electrostatic forces. In this sense, solid state physics is no longer fundamental; nowadays it is only in cosmology, astrophysics and high energy physics that we believe the fundamental laws are still unknown.

It is commonly said that most solids are crystalline; in the sense of the traditional solid–liquid–gas classification of matter this is true. Solids that have a sharp first order transition* to a liquid or vapour phase *are* crystalline in the sense that their atomic structure is based on a regularly repeated pattern, a sort of three-dimensional wallpaper, even if external crystalline form is not manifest. But many of the commonest solids—glass, plastics, wood, bone—are not so highly ordered and are not crystalline.

In this book we shall be concerned almost entirely with crystalline solids composed of one or a few types of atom, simply because this is the easiest problem, and the one with which most progress has been made. More complicated materials, particularly those of biological origin, we have

* i.e. one with a latent heat (see Mandl,[2] p. 233).

hardly begun to understand at the level of seeing how they can arise as solutions of Schrödinger's equation.

Even in the very restricted field of crystalline solids the most remarkable thing is the great variety of *qualitatively different* solutions to Schrödinger's equation that can arise. We have insulators, semiconductors, metals, superconductors—all obeying different macroscopic laws: an electric field causes an electric dipole moment in an insulator, a steady current in a metal or semiconductor and a steadily accelerated current in a superconductor. Solds may be transparent or opaque, hard or soft, brittle or ductile, magnetic or non-magnetic.

In discussing various types of solid we shall have occasion to speak of many different types of force or binding: ionic, metallic, covalant, van der Waals, exchange. But we must always remember that these terms are inventions of the human imagination, introduced as an aid to thought. *They are all consequences of the electrostatic interaction* between nuclei and electrons obeying Schrödinger's equation.* That these simple principles can lead to such a variety of consequences for the very simple systems we shall study may perhaps make it less incredible that the complex everyday world can also be a consequence of these same basic principles.

Our purpose in this chapter is to show how quantum mechanics leads to various types of chemical binding and a consequent variety of types of crystal structure. In section 1.2 we introduce a form of quantum mechanics that will be generally useful in this book and apply it to the simplest problem of chemical binding, H_2^+. The results are applied to a more qualitative discussion of the various types of binding in section 1.3, while the fundamentals are taken to greater depth in the optional section 1.4. Section 1.5 introduces the basic ideas of crystal geometry; these are not essential until Chapter 6, but some acquaintance with them is helpful in understanding the description in section 1.6 of various crystal structures we shall refer to later. We conclude this introductory chapter with a brief outline of x-ray crystallography in section 1.7, sufficient to suggest the experimental basis of the structures we have described.

1.2 INTERATOMIC FORCES

We know the stationary state solutions of the Schrödinger equation for an isolated atom (see, for example, Heitler[9]). What happens when two atoms approach each other closely? What do we mean by an interatomic force? As with any force, we infer its existence from the motion of the particles it acts on; since most of the mass of an atom is in the nucleus, it is essentially the motion of the atomic nuclei that concerns us.

* Also, of course, an invention of human imagination?