



# PHYSICAL PROPERTIES OF MATERIALS

M. C. LOVELL, A. J. AVERY, M. W. VERNON



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*PHYSICAL PROPERTIES OF MATERIALS*

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# Preface

Materials Science has now become established as a discipline in its own right as well as being of increasing importance in the fields of Physics, Chemistry and Engineering. To the student meeting this subject for the first time the combination of disciplines which it embraces represents a formidable challenge. He will require to understand the language of the physicist and chemist as well as appreciate the practical uses and limitations of solid materials. This book has been written as an introduction to the Physical Properties of Materials with these thoughts in mind. The mathematical content has been limited deliberately and emphasis is placed on providing a sound basis using simplified models. Once these are understood we feel that a mathematical approach is more readily assimilated and for this purpose supplementary reading is suggested. While the authors are deeply aware of the pitfalls in attempting such a treatment this is meant to be an essentially simple book to point the many avenues to be explored.

We anticipate that the book will appeal to first and second year degree students in a variety of disciplines and may not prove too difficult for those studying appropriate Higher National Certificate and Diploma courses. Electrical engineers working in the field of materials applications may well find it useful as a guide to modern thinking about materials and their properties.

The book begins with an introduction to some basic ideas of modern physics. The following three chapters discuss the structure of ideal and imperfect solids. They describe the techniques whereby samples of pure materials may be prepared in single crystal or amorphous forms and their structure determined. The mechanical properties of materials are surveyed in Chapter 5 and thermal properties in Chapter 6. Chapter 7 is devoted mainly to semiconducting materials but the usual introduction to semiconductor physics which is found in most texts on semiconductor devices has been omitted. Here much more emphasis has been placed on a survey of the physical properties of semiconducting materials including recent ideas and applications. The basic classical ideas of dielectrics are introduced in Chapter 8 followed by a discussion of piezoelectric, pyroelectric and ferroelectric materials. These materials are proving to have many varied and interesting possibilities for applications. A similar treatment is afforded to the magnetic and optical properties of solids in Chapters 9 and 10. New developments, for example magnetic bubbles and electro-optics are included and the relevant material properties presented. The final chapter is concerned with Superconductivity and attention is focused on materials which are being or may be used for superconducting devices.

For the materials scientist the aim of scientific theory is to predict new developments as well as explain experimental results, and a text such as this must point the way to new possibilities for materials. For this reason some exciting prospects for new materials are mentioned as well as new ideas which have not yet developed into

practical applications. By introducing the reader to the frontiers of the subject at one or two points his appetite may be whetted for scientific discovery in a rapidly developing field.

Throughout the book the MKS(SI) system of units has been used. References to appropriate review articles in the literature are cited so as to give the reader an opportunity to pursue a given topic. Examples are given at the end of most chapters and numerical answers are provided. These questions are designed to test and assist the student's understanding of the text.

We wish to thank Dr A. J. Woodall who gave us the opportunity to undertake the task of writing this book and to express gratitude to our colleagues who have helped in many and various ways. Particular thanks are due to Mr C. G. Wilson for his careful reading of the manuscript and helpful comments, and to Mr D. Carter for expert assistance with the illustrations. Finally we thank the Dean of the Royal Military College of Science for permission to publish.

*October 1975*

M. C. LOVELL  
A. J. AVERY  
M. W. VERNON

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# 1 Fundamentals

## 1.1 Introduction

In a treatment of the structure and properties of materials some basic ideas are needed concerning the properties of electrons in isolated atoms and in solids. In this chapter a few of these concepts are introduced briefly and simply. They include the wave mechanical picture of the atom, the idea of quantum numbers and the magnetic properties of atoms. Finally the energy band model for electrons in solids is introduced and the topic is more fully discussed in an Appendix.

## 1.2 Wave mechanics [1]

In the period between 1900 and 1927 a number of critical experiments involving both the interaction of light with matter and the behaviour of electrons were successfully interpreted in a new language, that of quantum mechanics. Light and electrons are now regarded as playing a dual role as wave and particle. A beam of light of frequency  $\nu$ , can be thought of as a stream of 'particles' or photons of energy  $h\nu$  where  $h$  is a constant and the intensity of the light is given by the density of photons, or in terms of the probability of finding a photon at a particular point. These probabilities are calculated by wave theory on the assumption that the probability is proportional to the square of the amplitude of the wave. Wave theory becomes a mathematical technique for calculating photon densities. A wave aspect can also be ascribed to particles with mass through the de Broglie relation. This suggests that a particle of mass  $m$  and velocity  $u$  has an associated wavelength  $\lambda$  given by

$$\lambda = h/mu = h/p, \quad (1.1)$$

where  $p$  is the particle momentum and  $h$  is Planck's constant. This constant, having the value  $6 \times 10^{-34}$  J s is the same as that occurring in the Planck relation linking the energy  $E$  of a photon with its frequency  $\nu$

$$E = h\nu. \quad (1.2)$$

The method of solving problems on an atomic scale through the wave aspects of particles (wave mechanics) was achieved by Schrödinger with his wave equation which in time dependent form is

$$\frac{h^2}{8\pi^2 m} \left( \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) = \frac{h}{2\pi j} \frac{\partial \psi}{\partial t} + V\psi. \quad (1.3)$$

This equation can be looked upon as a standard recipe for describing the wave aspects of a particle in terms of the amplitude of a *wave function*  $\psi$  of its coordinates in space and time  $x, y, z$  and  $t$ . In many cases the time can be separated as a trivial phase factor leaving the time independent form of the equation appropriate to a standing wave

$$\nabla^2 \psi(xyz) + \frac{8\pi^2 m}{h^2} (E - V) \psi(xyz) = 0, \quad (1.4)$$

where  $E$  is the total energy and  $V$  is the potential energy of the particle. The use of eqn (1.4) can best be illustrated by considering its application to one electron as in the hydrogen atom. The problem is defined by the forces acting on the electron described through the potential  $V$ , generally a function of the spatial coordinates  $x, y$  and  $z$ . The solution provides a knowledge of the energy  $E$  of the electron and the corresponding wave function  $\psi$  which is a mathematical function in space describing the three-dimensional wave pattern. Knowing  $\psi$ , the probability of finding the electron at a point is proportional to  $\psi^2$ . Wave mechanics indicates that in the hydrogen atom or any other atom, it is no longer permissible to think of an electron as describing an orbit in which its motion can be followed in detail. Only probabilities of finding the electron are significant and wave mechanics allows us to calculate these probabilities through a knowledge of  $\psi$  and hence  $\psi^2$ . In dealing with wave motion of light or sound the ideas of an amplitude and its square, the intensity of the wave, are familiar. A  $\psi$  pattern in one dimension could be just the simple one shown in Fig. 1.1 as a

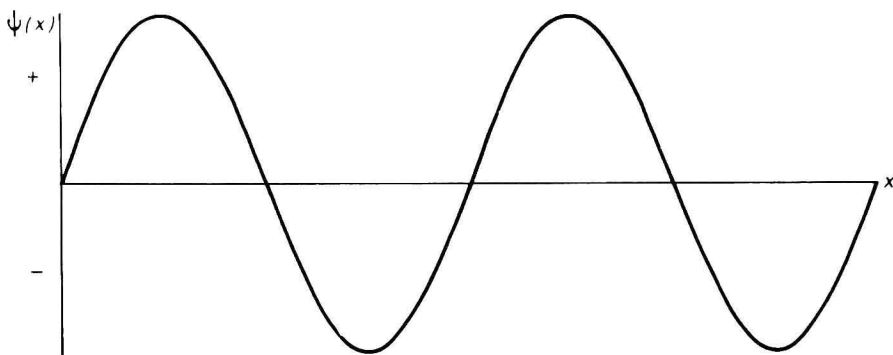


Fig. 1.1 Wave function  $\psi$  as a function of distance  $x$ .

function of coordinate  $x$ . This  $\psi$  has both a positive and negative part and so if it is to be interpreted as a probability it makes sense to take the square, since a negative probability has no meaning. If referred to a single particle, the value of  $\psi^2(x) dx$  given by the figure for any range  $dx$  is a measure of the probability of finding the particle in that range. Clearly if we sum  $\psi^2$  over the range of  $x$  from 0 to  $\infty$  the result must be unity if one particle is involved.

For most purposes, it is justifiable to regard an atom as consisting of a stationary nucleus of charge  $+Ze$  surrounded by a cloud of negative charge whose density at any point is proportional to the probability  $\psi^2$  of finding an electron at that point. This description of an electron cloud still allows the energy of an electron state, a stationary state, to be computed exactly. Just as a vibrating string can give rise to stationary vibrations or standing waves only if the wavelengths are related by whole numbers  $n$

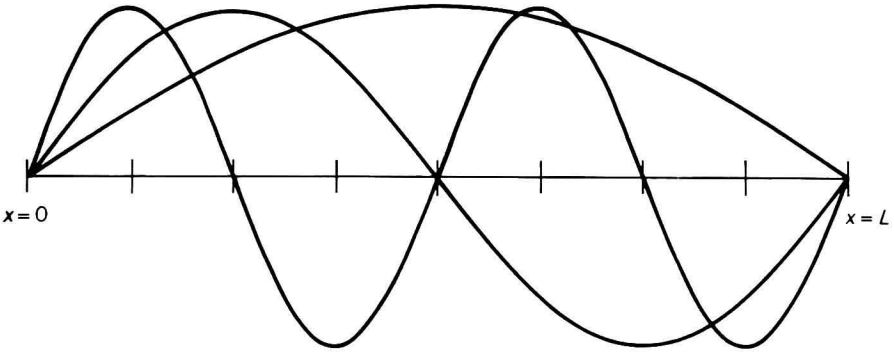


Fig. 1.2 Standing waves on a string of length  $L$  fixed at both ends.

to the length of the string (Fig. 1.2), so the wave equation (eqn (1.4)) for the motion of an electron round a nucleus can give rise to stationary states only if whole numbers are characteristics of the solution. The whole numbers are quantum numbers reminiscent of those in the work of Planck and Bohr which now turn up naturally from the solutions of the wave equation.

### 1.2.1 The hydrogen atom

Since the proton is so much heavier than the electron it can be considered as a fixed centre and the potential energy of the electron is therefore that due to a point charge  $+e$ . Instead of Cartesian coordinates, since the potential has a spherical symmetry, it is more convenient to use spherical coordinates  $r, \theta, \phi$  (Fig. 1.3).

The potential energy  $V$  is a function only of the distance  $r$  between the electron and the nucleus

$$V = -(e^2/4\pi\epsilon_0 r) \quad (1.5)$$

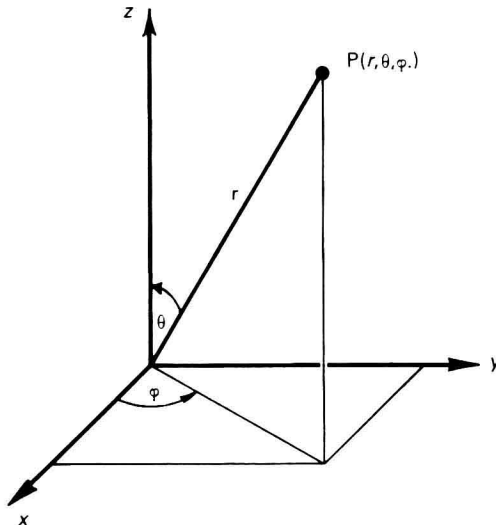


Fig. 1.3 Spherical polar coordinates  $r, \theta, \phi$ .



and eqn (1.4) becomes

$$\nabla^2 \psi(r, \theta, \phi) + \frac{2m}{\hbar^2} \left( E + \frac{e^2}{4\pi\epsilon_0 r} \right) \psi(r, \theta, \phi) = 0, \quad (1.6)$$

where the standard abbreviation  $\hbar = h/2\pi$  has been introduced. In polar coordinates the full expression looks formidable.

$$\nabla^2 \psi \equiv \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2}, \quad (1.7)$$

but the full equation can be solved exactly because  $\psi$  can be expressed as products of functions of the three variables  $r$ ,  $\theta$  and  $\phi$  and these can be solved for separately. So

$$\psi(r, \theta, \phi) = R(r)F(\theta)\Phi(\phi), \quad (1.8)$$

where  $R$  is a function of  $r$  only,  $F$  of  $\theta$  only and  $\Phi$  of  $\phi$  only. Each of these functions mirrors a motion of the electron in terms of the corresponding coordinate and each solution throws up its corresponding quantum number  $n$ ,  $l$  and  $m_l$ . These quantum numbers are not independent since although  $n$  can be any positive integer,  $l$  can only have one of the values  $0, 1, \dots, (n-1)$  and  $m_l$  can only have one of the values

$$m_l = -l, -(l-1), \dots, 0, \dots, (l-1), l.$$

Thus, for  $n = 1$ , only  $l = 0$  and  $m_l = 0$  are permitted while for  $n = 2$ ,  $l = 0$  (in which case  $m_l = 0$ ) or  $l = 1$  when  $m_l$  can be either  $-1, 0$  or  $+1$ . These rules result from the general boundary conditions imposed on  $\psi$  and do not arise from special assumptions for each particular problem.

The quantization which gives rise to  $m_l$  is the simplest case, since there is only one term in eqn (1.7) which involves  $\phi$ . The solution of the resulting differential equation is

$$\Phi(\phi) = A e^{im_l \phi}, \quad (1.9)$$

where  $A$  is a constant.

Now  $\Phi$  must have a definite unique value for a given  $\phi$  and so if that  $\phi$  is increased by any integral multiple of  $2\pi$ ,  $\Phi$  must remain the same. This is only so if  $m_l$  is an integer. Thus it is the mathematical condition on the uniqueness of  $\Phi$  which quantizes  $m_l$  and the same idea applies to  $n$  and  $l$ .

The quantum number  $n$  is called the principal or radial quantum number and  $1/n^2$  measures directly, in appropriate units, the energy of the electron in its orbit.  $l$  is the orbital or azimuthal quantum number and measures the angular momentum of the electron motion. The state for which  $l = 0$  is not one for which the electron is at rest but rather one in which the motion is as likely to be in one direction as another, leading to an angular momentum which on the average is zero. Electron angular momentum has the value  $l\hbar$ ,  $\hbar$  being the basic quantized unit.

For historical reasons, states for which  $l = 0, 1, 2, 3, 4, 5$ , etc. are called  $s, p, d, f, g, h$ , etc. The third or magnetic quantum number  $m_l$  measures the component  $m_l \hbar$  of angular momentum in a specified direction and describes the distribution of  $\psi$  about the  $z$  axis (Fig. 1.4). As long as the  $z$  axis remains undefined, states of different  $m_l$  are indistinguishable.

If however a specific direction is imposed on the atom from outside by application of a magnetic field, a direction is pointed in space and  $m_l$  becomes significant. This signposting by a magnetic field is possible because of the magnetic properties of the electron in its orbit. It acts like a small magnet which interacts with the magnetic field