

Materials Science

Third edition

© 1985 J.C. Anderson, K.D. Leaver,
R.D. Rawlings and J.M. Alexander

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PREFACE

This edition represents a general updating and revision of the text of the second edition to take account of continuing developments in the field of materials science and the helpful comments and criticisms that we have received from our colleagues around the world.

Chapter 7, on thermodynamics, has been revised and extended to include the basic ideas of lattice waves and this is applied, in the chapter on electrical conductivity, to phonon scattering of electrons.

Chapters 8 and 9 on mechanical properties have been revised and extended and the fundamental principles of the relatively new subject of fracture toughness have been introduced; the microstructural aspects of fracture, creep and fatigue, together with the interpretation of creep and fatigue data, are dealt with in more detail.

The section on steel in Chapter 10 has been considerably extended. A completely new chapter on ceramics and composites has been added to take account of the increasing development and importance of these materials.

The chapter on semiconductors has been revised and updated by including the field effect transistor. An innovation is the introduction of a complete new chapter on semiconductor processing which is an important area of application of materials science in modern technology.

The addition of a chapter on optical properties has given us the opportunity of discussing the principles of spectroscopy, absorption and scattering, optical fibre materials and laser materials.

In general, all chapters have been reviewed and minor revision, correction and updating has been carried out where required.

J.C.A.

K.D.L.

R.D.R.

J.M.A.

Preface to the first edition

The study of the science of materials has become in recent years an integral part of virtually all university courses in engineering. The physicist, the chemist, and the metallurgist may, rightly, claim that they study materials scientifically, but the reason for the emergence of the 'new' subject of materials science is that it encompasses all these disciplines. It was with this in mind that the present book was written. We hope that, in addition to providing for the engineer an introductory text on the structure and properties of engineering materials, the book will assist the student of physics, chemistry, or metallurgy to comprehend the essential unity of these subjects under the all-embracing, though ill-defined, title 'Materials science'.

The text is based on the introductory materials course which was given to all engineers at Imperial College, London. One of the problems in teaching an introductory course arises from the varying amounts of background knowledge possessed by the students. We have, therefore, assumed only an elementary knowledge of chemistry and a reasonable grounding in physics, since this is the combination most frequently encountered in engineering faculties. On the other hand, the student with a good grasp of more advanced chemistry will not find the treatment familiar and therefore dull. This is because of the novel approach to the teaching of basic atomic structure, in which the ideas of wave mechanics are used, in a simplified form, from the outset. We believe that this method has several virtues: not only does it provide for a smooth development of the electronic properties of materials, but it inculcates a feeling for the uncertainty principle and for thinking in terms of probability, which are more fundamental than the deterministic picture of a particle electron moving along a specific orbit about the nucleus. We recognize that this approach is conceptually difficult, but no more so than the conventional one if one remembers the 'act of faith' which is necessary to accept the quantization condition in the Bohr theory. The success of this approach with our own students reinforces the belief that this is the right way to begin.

In view of the differences which are bound to exist between courses given in different universities and colleges, some of the more advanced material has been separated from the main body of the text and placed at the end of the appropriate chapter. These sections, which are marked with an asterisk, may, therefore, be omitted by the reader without impairing comprehension of later chapters.

In writing a book of this kind, one accumulates indebtedness to a wide range of people, not least to the authors of earlier books in the field. We particularly wish to acknowledge the help and encouragement given by our

academic colleagues.

Our students have given us much welcome stimulation and the direct help of many of our graduate students is gratefully acknowledged. Finally, we wish to express our thanks to the publishers, who have been a constant source of encouragement and assistance.

J.C.A.

K.D.L.

Preface to the second edition

The goals of the first edition remain unchanged, but the need was felt to provide in the second edition a wider and more detailed coverage of the mechanical and metallurgical aspects of materials. Accordingly we have extensively rewritten the relevant chapters, which now cover mechanical properties on the basis of continuum theory as well as explaining the microscopic atomic mechanisms which underlie the macroscopic behaviour. The opportunity has also been taken to revise other chapters in the light of the many helpful comments on the first edition which we have received from colleagues around the world. We would like to thank here all who have taken the trouble to point out errors and inconsistencies, and especially our colleagues who have read the manuscript of this and the first edition. We are also indebted to Dr. D.L. Thomas and Dr. F.A.A. Crane for several micrographs which appear here for the first time.

J.C.A.

K.D.L.

J.M.A.

R.D.R.

SELF-ASSESSMENT QUESTIONS

A series of self-assessment questions, with answers, will be found at the end of each chapter. By using these the student can easily test his understanding of the text and identify sections that he needs to re-read. The questions are framed so that the answer is a choice between two or more alternatives and the answer is simply a letter A, B, C, etc. The correct answers are given at the end of each set of questions and it should be noted that, where a question involves more than two possibilities, there may be more than one right answer.

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BUILDING BLOCKS: THE ELECTRON

1-1 Introduction

Science is very much concerned with the identification of patterns, and the recognition of these patterns is the first step in a process that leads to identification of the building bricks with which the patterns are constructed. This process has all the challenge and excitement of exploration combined with the fascination of a good detective story and it lies at the heart of materials science.

At the end of the nineteenth century a pattern of chemical properties of elements had begun to emerge and this was fully recognized by Mendelée'ev when he constructed his periodic table. Immediately it was apparent that there must be common properties and similar types of behaviour among the atoms of the different elements and the long process of understanding atomic structure had begun. There were many wonders along the way. For instance, was it not remarkable that *only* iron, nickel, and cobalt showed the property of ferromagnetism? (Gadolinium was a fourth ferromagnetic element discovered later.) A satisfactory theory of the atom must be able to explain this apparent oddity. Not only was magnetism exclusive to these elements, but actual pieces of the materials sometimes appear magnetized and sometimes do not, depending on their history. Thus a theory that merely states that the atoms of the element are magnetic is not enough; we must consider what happens when the atoms come together to form a solid.

Similarly, we wonder at the extraordinary range-and beauty-of the shapes of crystals; here we have patterns-how can they be explained? Why are metals ductile while rocks are brittle? What rules determine the strength of a material and is there a theoretical limit to the strength? Why do metals conduct electricity while insulators do not? All these questions are to do with the properties of aggregations of atoms. Thus an understanding of the atom must be followed by an understanding of how atoms interact when they form a solid because this must be the foundation on which explanations of the properties of materials are based.

This book attempts to describe the modern theories through which many of these questions have been answered. We are not interested in tracing their history of development but prefer to present, from the beginning, the quantum-mechanical concepts that have been so successful in modern atomic theory. The pattern of the book parallels the pattern of understanding outlined above. We must start with a thorough grasp of fundamental atomic theory and go on to the theories of aggregations of atoms. As each theoretical concept emerges it is used to explain relevant observed properties. With such

a foundation the electrical, mechanical, thermal, and other properties of materials can be described, discussed, and explained.

To begin at the beginning we consider the building bricks of the atoms themselves, starting with the electron.

1.2 The electron

The electron was first clearly identified as an elementary particle by J. J. Thomson in 1897. A more detailed description of his experiment is given towards the end of this chapter; here it is sufficient to say that he was able to conclude that the electron is a constituent of all matter. It was shown to have a fixed, negative charge, e , of 1.6021×10^{-19} coulomb and a mass of 9.1085×10^{-31} kilogramme at rest. Thomson's proof of the existence of the electron was the essential prerequisite for the subsequent theories of the structure of the atom. However, before going on to consider these we must first review some of the known facts about atoms themselves.

1.3 Avogadro's number

In the electrolysis of water, in which a voltage is applied between two electrodes immersed in the water, hydrogen is observed to be given off at the negative electrode (the cathode). This indicates that the hydrogen ion carries a positive charge and measurement shows that it takes 95,650 coulombs of electricity to liberate one gramme of hydrogen. Now if we know how many atoms of hydrogen make up one gramme it would be possible to calculate the charge per hydrogen ion. This can be done using Avogadro's number, but before defining it we must describe what is meant by a 'gramme-atom' and a 'gramme-molecule' (or 'mol').

It is known from chemistry that all substances are either elements or compounds and that compounds are made up of elements. Any quantity of an element is assumed to be made up of atoms, all of equal size and mass, and the mass of each atom when expressed in terms of the mass of the hydrogen atom was defined as its atomic weight. In 1815 Prout suggested that if the atomic weight of hydrogen were taken as unity the atomic weights of all other elements should be whole numbers. This turned out not to be quite true and internationally agreed atomic weights were based, instead, on the atomic weight of oxygen being 16, which gives hydrogen the atomic weight 1.0080. It was later discovered that an element could have different isotopes, i.e., atoms of the same atomic number could have differing atomic weights: this will be discussed in a later chapter. Mixtures of naturally occurring isotopes were the cause of the atomic weights not being exactly whole numbers. In 1962 it was internationally agreed to use the isotope ^{12}C , with an atomic weight of 12, as the basis of all atomic weights, which still gives to hydrogen the value 1.0080.

Thus a gramme-atom of a substance is the amount of substance whose mass in grammes equals its atomic weight. Similarly a gramme-molecule (or mol) of a compound is the amount whose mass in grammes equals its

molecular weight which, in turn, is the sum of the atomic weights of the atoms which go to make up the molecule.

We may now define Avogadro's number, which is the number of atoms in a gramme-atom (or molecules in a gramme-molecule) of any substance and it is a universal constant.

Returning to our electrolysis experiment, the amount of electricity required to liberate a gramme-atom of hydrogen will be $95,650 \times 1.0080 = 96,420$ coulombs. Now, suppose we *assume* that the charge on the hydrogen ion is equal to that on the electron, then we may calculate Avogadro's number, N .

$$N = \frac{96,420}{1.602 \times 10^{-19}} = 6.02 \times 10^{23} \text{ mol}^{-1}$$

Experimentally, the accurate value has been determined as 6.023×10^{23} and so it may be concluded that the charge on the hydrogen ion is equal in magnitude and opposite in sign to that on the electron.

Also using Avogadro's number we may calculate the mass of a hydrogen atom as

$$\begin{aligned} \frac{\text{Atomic weight}}{\text{Avogadro's number}} &= \frac{1.0080}{6.023 \times 10^{23}} \\ &= 1.672 \times 10^{-24} \text{ gramme} \end{aligned}$$

This is just 1,840 times the mass of the electron.

Such a calculation suggests that there is another constituent of atoms, apart from the electron, which is relatively much more massive and which is positively charged.

1.4 The Rutherford atom

In 1911 Rutherford made use of the α -particle emission from a radioactive source to make the first exploration of the structure of the atom. By passing a stream of particles through a thin gold foil and measuring the angles through which the beam of particles was scattered he was able to conclude that most of the mass of the gold atom (atomic weight 187) resided in a small volume called the nucleus which carried a positive charge. He was also able to show that the radius of the gold nucleus is not greater than 3.2×10^{-12} cm.

Since the number of gold atoms in a gramme-molecule of gold is given by Avogadro's number and, from the density (mass per unit volume) we may calculate the volume occupied by a gramme-molecule, then we may make an estimate of the volume of each atom. If we assume them to be spheres packed together as closely as possible we can deduce that the radius of the gold atom is in the region of 10^{-8} cm, which is 10,000 times larger than the radius obtained by Rutherford. Thus the atom seems to comprise mainly empty space.

To incorporate these findings and the discovery of the electron Rutherford proposed a 'planetary' model of the atom; this postulated a small dense

nucleus carrying a positive charge about which orbited the negative electrons like planets round the sun. The positive charge on the nucleus was taken to be equal to the sum of the electron charges so that the atom was electrically neutral.

This proposal has an attractive simplicity. Referring to Fig. 1.1: if the electron moves in a circular orbit of radius, r , with a constant linear velocity, v , then it will be subject to two forces. Acting inwards will be the force of electrostatic attraction described by Coulomb's law:

$$F = \frac{q_1 q_2}{4\pi\epsilon_0 r^2} \quad (1.1)$$

where q_1 and q_2 are the positive and negative charges, in this case each having the value of the charge, e , on the electron and ϵ_0 is the permittivity of free space given by $10^{-9}/36\pi$.

Acting outwards there will be the usual centrifugal force given by mv^2/r , where m is the electron mass and v^2/r is its radial acceleration. The orbit of the electron will settle down to a stable value where these two forces just balance each other, that is, when

$$\frac{mv^2}{r} = \frac{e^2}{4\pi\epsilon_0 r^2} \quad (1.2)$$

Unfortunately, this model has a basic flaw. Maxwell's equations, which describe the laws of electromagnetic radiation, can be used to show that an electron undergoing a change in velocity (i.e., acceleration and deceleration) will radiate energy in the form of electromagnetic waves. This can be seen by analogy: if the electron in a circular orbit were viewed from the side it would appear to be travelling rapidly backwards and forwards. Now it carries a charge and a moving charge represents an electric current. Thus its alternating motion corresponds to an alternating electric current at a very high frequency. Just such a high-frequency alternating current is supplied to an aerial by a radio transmitter and the electromagnetic radiation from the aerial is readily detectable. Thus we must expect the electron in Rutherford's model of the atom continuously to radiate energy. More formally, since an electron moving in an orbit of radius, r , with a linear velocity, v , is, by the laws of Newtonian mechanics, subject to a continual radial acceleration of magnitude v^2/r , it must, by the laws of electromagnetic radiation, continuously radiate energy.

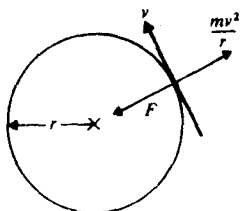


Fig. 1.1 Rutherford's planetary atomic model

The kinetic energy of the electron in its orbit is proportional to the square of its velocity and if it loses energy its velocity must diminish. The centrifugal force, mv^2/r , due to the radial component of acceleration will therefore also diminish and so the electrostatic attraction between the positive nucleus and the negative electron will pull the electron closer to the nucleus. It is not difficult to see that the electron would ultimately spiral into the nucleus.

The resolution of this difficulty was only made possible by the bringing together of a variety of observations and theories and we must now consider these briefly in turn.

1-5 Waves and particles

One of the more remarkable puzzles which gradually emerged from experimental physics as more and more physical phenomena were explored was that it appeared that light, which was normally regarded as a wave (an electromagnetic wave to be precise), sometimes behaved as if the ray of light were a stream of particles. Similarly, experimental evidence emerged suggesting that electrons, which we have so far treated as particles, may behave like waves. If this is so, the Rutherford atom, based on treating the electron as a particle having a fixed mass and charge and obeying Newtonian mechanics, is evidently too crude a model. This is obviously a crucial matter and we must examine the relevant experiments carefully.

1-5-1 Electron waves

Remember that the properties which convince us that light is a wave motion are *diffraction* and *interference*. For instance, a beam of light impinging on a very narrow slit is diffracted (i.e., spreads out behind the slit). A beam of light shining on two narrow adjacent slits, as shown in Fig. 1-2, is diffracted and if a screen is placed beyond the slits interference occurs, giving a characteristic intensity distribution as shown. Yet another pattern is produced if we use many parallel slits, the device so produced being called a *diffraction grating*. As shown in Fig. 1-3, if we take a line source of light and observe the image it produces when viewed through a diffraction grating we see a set of lines whose separation depends on the wavelength of the light and the

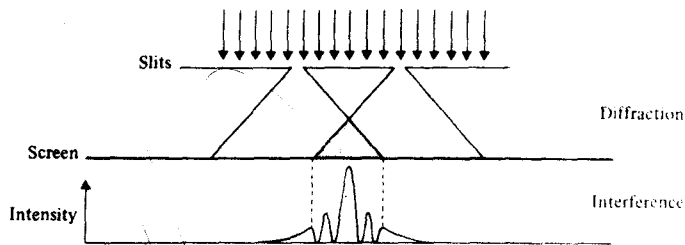


Fig. 1-2 Diffraction of light through two slits