



**IOM
FACSIMILE
REPRINTS**

THE STRUCTURE OF METALS AND ALLOYS

R E SMALLMAN W HUME-ROTHERY

C W HAWORTH

**FIRST
PUBLISHED
1936**



The Institute of Metals

TG 111
H922

9060094
9050094

THE STRUCTURE OF METALS AND ALLOYS



E9060094

WILLIAM HUME-ROTHERY

*Late Isaac Wolfson Professor in Metallurgy,
University of Oxford*

R. E. SMALLMAN

*Professor of Physical Metallurgy,
University of Birmingham*

and

C. W. HAWORTH

*Department of Metallurgy,
University of Sheffield*



Monograph and Report Series

No. 1

1969

The Metals and Metallurgy Trust
of the
Institute of Metals and the Institution of Metallurgists
17 BELGRAVE SQUARE, LONDON, S.W.1

Book 423
ISBN 0 901462 38 1

EDITION	AUTHOR(S)
<i>First edition</i>	<i>March 1936</i>
<i>Second printing</i>	<i>January 1938</i>
<i>Third printing (revised)</i>	<i>May 1939</i>
<i>Second edition</i>	<i>January 1944</i> W. Hume-Rothery
<i>Fifth printing</i>	<i>October 1945</i>
<i>Sixth printing (revised)</i>	<i>December 1947</i>
<i>Seventh printing (revised)</i>	<i>February 1950</i>
<i>Third edition (greatly enlarged)</i>	<i>March 1954</i>
<i>Ninth printing (revised)</i>	<i>July 1956</i> W. Hume-Rothery and G.V. Raynor
<i>Fourth edition (revised)</i>	<i>March 1962</i>
<i>Fifth edition (revised)</i>	<i>February 1969</i> W. Hume-Rothery, R.E. Smallman and C.W. Haworth

Facsimile reprint published in 1988 by

The Institute of Metals
1 Carlton House Terrace
London SW1Y 5DB
and

The Institute of Metals North American Publications Center
Old Post Road Brookfield VT05036 USA

© THE INSTITUTE OF METALS 1988
ALL RIGHTS RESERVED

British Library Cataloguing in Publication Data
Hume-Rothery, William, 1899-1968

The structure of metals and alloys. –
5th ed. (rev.)

1. Metals, Structure

I. Title II. Smallman, R.E. (Raymond
Edward), 1929- III. Haworth, C.W. (Colin
William) IV. Institute of Metals (1985-)
669'.5

ISBN 0-901462-38-1

Library of Congress Cataloguing in Publication Data
applied for

First printed by Richard Clay (The Chaucer Press) Ltd,
Bungay, Suffolk

Reprinted in England by Antony Rowe Ltd,
Bumper's Farm, Chippenham, Wilts

THE STRUCTURE OF
METALS AND ALLOYS

FOREWORD TO REPRINT OF FIFTH EDITION

WHILE reappraising the likely value and usefulness of a reprint of this introductory textbook, it was inevitable that one should be impressed, yet again, by the clarity and style of the original writings of Professor W. Hume-Rothery (1899 – 1968). Over a very significant period of metallurgical history, he undertook the demanding task of spreading the word on a subject that forms the central ground of physical metallurgy. In the crucial third and fourth editions of 1954 and 1962, the enterprise was further strengthened and enhanced by his collaboration with Professor G.V. Raynor (1913 – 1983); these two versions provided a valuable introduction to the internal architecture of crystalline materials and were soon to be found on the bookshelves of metallurgists, physicists, chemists, and engineers throughout the world.

In the late 1960s, important advances in metallurgical science encouraged the idea of issuing a fifth edition. At that time Raynor was committed to a period of university higher administration and was unable to give sufficient time to the revision and so, together with Dr C.W. Haworth of the University of Sheffield, I was privileged to be asked to collaborate with Hume-Rothery in its preparation. By reducing the emphasis on ductile metals, such as copper, silver and gold, and by omitting the section on the ferrous alloys it was possible to introduce new facets and concepts without unduly increasing the size of the volume. The new sections provided opportunities for alloy theory to be updated and for exciting developments in the theory and imaging of dislocations to be introduced. Naturally, attempts were made to comply with the spirit and sense of progression that was so evident in earlier editions.

Now, nearly twenty years after its first appearance, it has been decided to reprint the fifth edition. The front line of research has moved on and more recent treatments of alloy theory are likely to include discussion of superconductive Chevrel phases and Darken-Gurry mapping. Nowadays a much more powerful armoury of techniques is available to the researcher. Thus, computer-aided methods are used for elucidating and predicting alloy structures and associated phase diagrams. For synthesis, extremely rapid rates of melt cooling, in the order of 10^6 degK s^{-1} , enable metastable 'glassy' alloys to be produced which combine elements in concentrations hitherto thought impossible according to the original 'rules' of alloying. Modern precision in planar composite alloying is exemplified by the use of molecular beam epitaxy to deposit 'modulated' superconductive compounds, layer by layer. Techniques for the assessment of microstructure and microanalysis have been developed to a sophisticated degree arising from the interaction of electrons with matter, namely Auger spectroscopy, SEM and TEM with associated analytic facilities of back scattering, X-ray analysis (EDX),

energy loss spectroscopy (EELS), and convergent beam diffraction (CBDPs). The same electron-analytical techniques that are used to characterise such finely-crafted structures have also enabled the theory of dislocations to be consolidated and extended considerably since 1969. In particular, it has been possible to discriminate with greater precision between stacking fault energy values of different alloy structures and to appreciate the importance of these differences.

These advances, both theoretical and practical, build upon rather than undermine the ideas expressed in this book. Certain peripheral statements might be questioned but that is to be expected in scientific activities. As indicated in a comprehensive review of the electronic properties of Hume-Rothery phases by Massalski and Mizutani*, the Hume-Rothery rules are still capable of prompting and stimulating useful scientific debate. Against this background, I believe this book has a part to play in 'setting the scene' for students and researchers alike; some nuggets still remain to be found in its pages.

R E SMALLMAN

*T.B. Massalski & U. Mizutani, *Prog. Mat. Sci.*, 22 (1978); 151-262.

PREFACE TO 1969 EDITION

THE first edition of this monograph (1936) contained a certain amount of original generalization, and was intended both for students and research workers. The book has always been maintained at an elementary level, and, with the tremendous advances in the science of metals since the original edition, an increasing selectivity in subject matter has been necessary. As well as appealing to students at universities and technical colleges, it is hoped that the book will be a useful source of information to those whose work requires occasional reference to alloy formation or fundamental aspects of lattice imperfections in real metals.

The preparation of this fifth edition has involved a reconsideration of the contents of the book, in addition to changes required by recent developments. The section on terminal solid solutions no longer takes the form of a detailed discussion of copper, silver, and gold alloys, work on which formed the origin of our understanding of this field, but consists of a more general discussion based on the factors that control this aspect of alloy formation. Similarly, our understanding of intermediate phase formation has developed so that we can now base consideration of this subject on the fundamental problem of arranging atoms in an economical space-filling structure, with due attention to electronic effects, and Part V has been rewritten from this viewpoint. The special section on the alloys of iron, which was included in some previous editions, has been omitted, since it was felt that in the space available insufficient justice could be done to this subject, which in any case has been dealt with more comprehensively in another text.

The greatest advances in the science of metals have been in connection with imperfections in crystals and the development of the theory of dislocations. The final section of the book (Part VI) has been completely rewritten, and gives an account of the essential theoretical features of imperfections, together with a discussion of the dislocations found in different crystalline structures.

Professor Hume-Rothery, who until his retirement in 1966 was the Isaac Wolfson Professor of Metallurgy at the University of Oxford, died in the final stages of the preparation of this new edition. Throughout his life, as well as being a leading figure in work directed towards an understanding of the basis of alloy behaviour, Professor Hume-Rothery devoted himself to the writing of books on the subject. He was the sole author of the original edition of this book, which when published in 1936 was the first text-book of its kind, and co-author with Professor

Preface to 1969 Edition

G. V. Raynor (Faculty of Science and Engineering, University of Birmingham) of more recent editions. We are indeed honoured to have had the opportunity of collaborating with Professor Hume-Rothery in revising this edition of his book.

We acknowledge with gratitude the great help we have received from discussion with our respective colleagues.

C. W. HAWORTH,
*Department of Metallurgy,
University of Sheffield.*

R. E. SMALLMAN,
*Department of Physical Metallurgy
and Science of Materials,
University of Birmingham.*

CONTENTS

PREFACE	vii
PART I. THE ELECTRONIC BACKGROUND TO METALLURGY:	
1. The Structure of the Atom	1
2. The Structure of the Molecule	16
3. The Structure of the Crystal	24
4. Electron Theory of Alloys	41
PART II. THE CRYSTAL STRUCTURES OF THE ELEMENTS	
	47
PART III. THE ATOMIC RADII AND SOME PHYSICAL PROPERTIES OF THE ELEMENTS	
	71
PART IV. TERMINAL SOLID SOLUTIONS:	
1. Introduction	110
2. Free Energy and Solid Solubility	111
3. Composition Disorder in Solid Solutions	117
4. Displacement Disorder in Solid Solutions	121
5. The Concept of Atomic Size-Factor	124
6. The Electronegative Valency Effect	128
7. Relative Valency Effects	132
8. Liquidus and Solidus Curves	135
9. The Form of Primary Solid-Solubility Curves	147
10. Superlattice Structures	163
11. The Theory of Superlattice Formation	178
12. Ternary Solid Solutions	187
13. Lattice Spacings of Terminal Solid Solutions	191
PART V. INTERMEDIATE PHASES IN ALLOY SYSTEMS:	
1. Introduction	203
2. Atomic-Packing and Space-Filling Considerations	207
3. Normal Valency Compounds	213
4. Electron Compounds of Copper, Silver, and Gold	227
5. Transition-Metal Phases	239
6. Interstitial Phases, and Other Structures Determined by the Size-Factor	260
PART VI. IMPERFECTIONS IN CRYSTALS:	
1. Introduction	287
2. Plastic Deformation of Crystals	289
3. Theoretical Strength of Crystals	291
4. The Concept of a Dislocation	292
5. Burgers Vector and Circuit	294
6. Dislocation Glide and Climb	295
7. Conservative and Non-Conservative Motion	297

Contents

PART VI. IMPERFECTIONS IN CRYSTALS (*contd.*):

8. Elasticity Properties of a Dislocation	300
9. Origin of Dislocations	305
10. Observations of Crystal Imperfections	310
11. Dislocations and Stacking Faults in Typical Metallic Structures	318
12. Defects in Intermetallic and Non-Metallic Crystals	345
13. The Strengthening of Metals	358
14. Annealing of Metals	386
NAME INDEX	399
SUBJECT INDEX	402

PLATES

I-IV. *Between pp. 48 and 49*
V-XX. *Between pp. 296 and 297*

PART I. THE ELECTRONIC BACKGROUND TO METALLURGY.

1. THE STRUCTURE OF THE ATOM.

The development of the modern theory of metals and alloys coincided with great advances in the theory of atomic structure, and although the space available does not enable us to deal with this subject in any detail, we shall describe certain points in order to indicate the general outlook, and to introduce terms with which the metallurgical reader may not be familiar. For this purpose we shall deal first with the structure of the free atom, and then with the forces which come into play when the atoms are bound together to form molecules, and finally with the relation between these forces and those which hold the atoms or molecules together in a solid crystal.

In Fig. I.1 is shown the Periodic Table of the Elements, and we shall assume a general knowledge of the valency relations of inorganic chemistry. The work of Rutherford, Soddy, Moseley, Russell, Fajans, and others led gradually to the concept of a nuclear atom consisting of a minute positively-charged nucleus surrounded by a sufficient number of electrons to keep the atom as a whole neutral. The dimensions of the nucleus are of the order of 10^{-12} cm, and are thus very small compared with the distances between atoms in molecules and crystals, which are of the order of 10^{-8} cm., but the nucleus contains almost the whole mass of the atom. The region occupied by the surrounding electrons is of the order of 10^{-7} to 10^{-8} cm, and is thus of the same magnitude as the interatomic distances in crystals. The charge on the nucleus is $+Ze$, where $-e$ is the charge on one electron, and Z , the so-called atomic number, gives the position of the element in the Periodic Table. Since the atom as a whole is neutral, an atom of atomic number Z is surrounded by Z electrons, so that an atom of, say, silver of atomic number 47, contains a nucleus with a charge of $+47e$, surrounded by 47 electrons.

In the reactions of ordinary physics, chemistry, and metallurgy the nucleus of an atom is indestructible, and the atomic number is the quantity which determines the chemical characteristics. Thus, in the case of iron, cobalt, and nickel, the atomic numbers are 26, 27, and 28, respectively, and chemical characteristics show that this is the correct order of these three elements in the Periodic Table, although the atomic weights are 55.85, 58.93, and 58.71. Cobalt and nickel are thus out of

place as regards atomic weight, although in place as regards atomic number, the latter quantity being first determined by Moseley by the study of X-ray spectra. Tellurium (atomic weight 127.60, atomic

H 1																He 2						
Li 3		Be 4		B 5		C 6		N 7		O 8		F 9		Ne 10								
Na 11		Mg 12		Al 13		Si 14		P 15		S 16		Cl 17		Ar 18								
K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36					
Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54					
Cs 55	Ba 56	La 57	Ce 58	Pr 59	•• 60	Yb 70	Lu 71	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86
Fr 87	Ra 88	Ac 89	Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102							

FIG. I.1. Periodic Table of the elements.

number 52) and iodine (atomic weight 126.90, atomic number 53) provide a further example of this kind.

Although the nuclei are indestructible in ordinary chemical reactions, the study of the radioactive elements showed that the nuclei of the

heaviest atoms could undergo spontaneous disintegration with the emission of α -rays or α -particles, which were identified as doubly charged helium He^{++} ions, or of β -rays, which are ordinary negatively charged electrons, or alternatively of γ -rays, which have no charge or mass but are analogous to very hard X-rays (i.e. X-rays of very short wave-length). If an atom undergoes an α -ray disintegration, the expulsion of the He^{++} ion removes two positive charges and four units of mass from the nucleus, and so produces an atom of an element lying two places earlier in the Periodic Table, and of atomic weight 4 units lower than that of the parent element. In a β -ray disintegration the removal of one negative charge e from the nucleus increases its positive charge by $+e$, and so produces an element lying one place forward in the Periodic Table compared with the parent element, but of the same atomic weight.* A γ -ray disintegration removes neither mass nor charge from the nucleus, and so leaves the atom in the same position in the Periodic Table.

The study of these transformations by Soddy led to the discovery of elements whose atoms had the same atomic number, but different atomic weights, and these are called *isotopes*, because they occupy the same place in the Periodic Table. The later work of Aston showed that this phenomenon was quite general, and that nearly all elements were mixtures of isotopes, the observed atomic weight of an element being the weighted average of that of its isotopes, the relative proportions of which varied from one element to another. To a first approximation, the atomic weights of the isotopes were whole numbers on the hydrogen scale, and this led to the conclusion that the nuclei themselves were built up from fundamental units. This work naturally suggested the possibility that the nuclei of lighter elements might be broken up, and the artificial disintegration of atomic nuclei was first carried out on a small scale by Rutherford and his collaborators, who used the α -rays from radioactive elements to bombard the atoms of lighter elements. In this way the science of nuclear physics was developed in which one kind of element could be prepared from another, and the work culminated in the various atomic-energy projects of today. This has led to the preparation of the new *trans-uranic elements* which do not occur naturally on the Earth, and which lie beyond uranium in the Periodic Table.

If the data in Table I are examined it will be seen that the atomic weights of the lighter elements are roughly double the atomic numbers, whilst in the heavier elements the atomic weight is relatively greater. It was first shown by Chadwick that, when beryllium is bombarded by

* We are here ignoring the mass of the electron, which is only $1/1830$ that of a hydrogen atom.

TABLE I. *Relative Atomic Weights, 1965.*Based on the atomic mass of $^{12}\text{C} = 12$.

	Sym- bol	At. No.	At. Wt.*		Sym- bol	At. No.	At. Wt.*
Actinium .	Ac	89	[227]	Mercury .	Hg	80	200.59
Aluminium .	Al	13	26.9815	Molybdenum .	Mo	42	95.94
Americium .	Am	95	[243]	Neodymium .	Nd	60	144.24
Antimony .	Sb	51	121.75	Neon .	Ne	10	20.183
Argon .	A	18	39.948	Neptunium .	Np	93	[237]
Arsenic .	As	33	74.9216	Nickel .	Ni	28	58.71
Astatine .	At	85	[210]	Niobium .	Nb		
Barium .	Ba	56	137.34	(Columbium)	(Cb)	41	92.906
Berkelium .	Bk	97	[249]	Nitrogen .	N	7	14.0067
Beryllium .	Be	4	9.0122	Nobelium .	No	102	[254]
Bismuth .	Bi	83	208.980	Osmium .	Os	76	190.2
Boron .	B	5	10.811†	Oxygen .	O	8	15.9994
Bromine .	Br	35	79.904	Palladium .	Pd	46	106.4
Cadmium .	Cd	48	112.40	Phosphorus .	P	15	30.9738
Caesium .	Cs	55	132.905	Platinum .	Pt	78	195.09
Calcium .	Ca	20	40.08	Plutonium .	Pu	94	[242]
Californium .	Cf	98	[251]	Polonium .	Po	84	[210]
Carbon .	C	6	12.01115	Potassium .	K	19	39.102
Cerium .	Ce	58	140.12	Praseodymium	Pr	59	140.907
Chlorine .	Cl	17	35.453	Promethium .	Pm	61	[147]
Chromium .	Cr	24	51.996	Protactinium .	Pa	91	[231]
Cobalt .	Co	27	58.9332	Radium .	Ra	88	[226]
Copper .	Cu	29	63.546	Radon .	Rn	86	[222]
Curium .	Cm	96	[247]	Rhenium .	Re	75	186.2
Dysprosium .	Dy	66	162.50	Rhodium .	Rh	45	102.905
Einsteinium .	Es	99	[254]	Rubidium .	Rb	37	85.47
Erbium .	Er	68	167.26	Ruthenium .	Ru	44	101.07
Europium .	Eu	63	151.96	Samarium .	Sm	62	150.35
Fermium .	Fm	100	[253]	Scandium .	Sc	21	44.956
Fluorine .	F	9	18.9984	Selenium .	Se	34	78.96
Francium .	Fr	87	[223]	Silicon .	Si	14	28.086
Gadolinium .	Gd	64	157.25	Silver .	Ag	47	107.868
Gallium .	Ga	31	69.72	Sodium .	Na	11	22.9898
Germanium .	Ge	32	72.59	Strontium .	Sr	38	87.62
Gold .	Au	79	196.967	Sulphur .	S	16	32.064†
Hafnium .	Hf	72	178.49	Tantalum .	Ta	73	180.948
Helium .	He	2	4.0026	Technetium .	Tc	43	[99]
Holmium .	Ho	67	164.930	Tellurium .	Te	52	127.60
Hydrogen .	H	1	1.00797	Terbium .	Tb	65	158.924
Indium .	In	49	114.82	Thallium .	Tl	81	204.37
Iodine .	I	53	126.9044	Thorium .	Th	90	232.038
Iridium .	Ir	77	192.2	Thulium .	Tm	69	168.934
Iron .	Fe	26	55.847	Tin .	Sn	50	118.69
Krypton .	Kr	36	83.80	Titanium .	Ti	22	47.90
Lanthanum .	La	57	138.91	Tungsten .	W	74	183.85
Lawrencium .	Lw	103	—	Uranium .	U	92	238.03
Lead .	Pb	82	207.19	Vanadium .	V	23	50.942
Lithium .	Li	3	6.939	Xenon .	Xe	54	131.30
Lutetium .	Lu	71	174.97	Ytterbium .	Yb	70	173.04
Magnesium .	Mg	12	24.312	Yttrium .	Y	39	88.905
Manganese .	Mn	25	54.9380	Zinc .	Zn	30	65.37
Mendelevium .	Md	101	[256]	Zirconium .	Zr	40	91.22

* A value given in brackets denotes the mass number of the isotope of longest known half-life, which is not necessarily the most important isotope in atomic-energy work.

† Because of natural variations in the relative abundance of their isotopes, the atomic weights of boron and sulphur have a range of ± 0.003 .

α -rays, particles are produced whose mass is equal to that of the nucleus of the hydrogen atom (this is called a *proton*), but which are electrically neutral. These particles were later produced in other ways, and are now known as *neutrons*. The development of nuclear physics led to the discovery of the neutron as a fundamental constituent of all atomic nuclei. An atom of atomic weight W and atomic number Z contains a nucleus of Z protons and $(W-Z)$ neutrons, and for the lighter elements for which $W \sim 2Z$ the numbers of protons and neutrons are about equal. The increase in the relative number of neutrons in the heavy elements is the result of the fact that, since the protons carry a charge of $+e$, they repel one another, whereas there is no electrostatic force between a neutron and a proton, or between two neutrons. An atom of a heavy element with equal numbers of protons and neutrons would be unstable because of the mutual repulsion of the protons, but the introduction of an excess of neutrons serves to dilute the protons, and so to preserve the stability of the atom.

Apart from neutrons and protons, the nuclei of atoms contain *mesons*, whose masses are of the order of 200–300 times that of an electron. These mesons are of different kinds and have charges of $+e$ or $-e$, whilst neutral mesons also exist. They give rise to fields which are not electrostatic in nature, and it is these meson fields which bind the protons and neutrons together in a nucleus. This kind of work lies outside the scope of the present book, and the reader may consult the works listed below.*

The structure of the nucleus is unimportant for most work in ordinary metallurgy, although the preparation of artificial isotopes has provided a useful method of studying processes such as self-diffusion in metals. In this kind of work, a thin layer of a radioactive isotope of a metal may be electroplated on to a specimen of the ordinary non-radioactive metal, and, after heating for a given time, the penetration of the radioactive isotope can be determined. With the release of information about atomic-energy work, problems are arising in which a knowledge of nuclear structure is essential to the metallurgist, but these are not considered in the present book.

* *Elementary :*

D. H. Frisch and A. M. Thorndyke, "Elementary Particles". 1963: New York (D. Van Nostrand).

Intermediate :

W. E. Burcham, "Nuclear Physics", 2nd edn. 1965: London (Longmans).

E. Segre, "Nuclei and Particles". 1964: New York (W. A. Benjamin, Inc.).

Advanced :

M. A. Preston, "Physics of the Nucleus". 1962: New York (Addison Wesley).

The first problem of extra-nuclear atomic structure was to determine the arrangement or grouping of the electrons around the nuclei of the different atoms, and here the clue was provided by the fact that elements with similar properties occur periodically in the Table of Fig. I.1. This clearly suggests that as we proceed along the Periodic Table, the addition of electrons takes place by the building up of a series of stable groups or shells, so that each time a group is completed the process begins again. The fact that the Short Periods contained eight elements, concluding with the inert gases, naturally suggested that eight electrons formed a stable group. The classification of electrons into groups was due primarily to the work of Bohr, with later modifications by Stoner and Main-Smith, and was based chiefly on the study of optical spectra interpreted in terms of the older quantum theory. The underlying assumption of this theory was that the electrons revolved round the nucleus in definite orbits which were called *stationary states*, and that the emission or absorption of radiation took place by an electron jumping from one stationary state to another. This concept of stationary states was in contradiction to the older Classical Mechanics, which would have allowed an infinite number of possible orbits. The original Bohr theory of circular orbits postulated that the only stationary states which were stable were those for which the angular momentum was an integral

multiple of $\frac{h}{2\pi}$, where h was a fundamental constant called Planck's

constant. In this way an electronic orbit or state came to be associated with a whole number, the so-called *quantum number*. An electron could, for example, revolve in an orbit for which the angular momentum was

$\frac{h}{2\pi}, \frac{2h}{2\pi}, \frac{3h}{2\pi} \dots$ or in general $\frac{nh}{2\pi}$, where n was the quantum number of the

orbit. The theory was then extended to elliptical orbits, for which each state is characterized by two quantum numbers. Of these, the principal quantum number n is a measure of the energy of the orbit; the negative energy varies inversely as n^2 , the energy being taken as zero for infinitely large n . The major axis of the ellipse is also proportional to n^2 , so that the orbits become larger with increasing n . The secondary quantum number k is a measure of the angular momentum associated

with the orbit, which is equal to $\frac{kh}{2\pi}$. The ratio k/n gives the ratio of the

minor to the major axis of the ellipse and thus determines its eccentricity.

In spite of its great success, the Bohr theory was not in complete agreement with the facts, and was logically unsatisfactory, since it assumed that, whilst the electron in its orbit obeyed the laws of classical mechanics, it was at the same time subject to the apparently arbitrary

quantum restrictions. This position suggested that, whilst the laws of classical mechanics were satisfactory for the mechanics of comparatively heavy bodies, they required modification when applied to the motion of an electron. The solution to this difficulty was found, not by making further arbitrary assumptions, but by recasting the laws of mechanics into a new framework, the so-called *wave mechanics* or *quantum mechanics*. The details of this work lie outside the scope of the present book, but the reader may note here that the first step was taken at the end of the eighteenth century by Hamilton, whose ideas were then developed further by de Broglie and Schrödinger in the years 1920-26. The problem of an electron moving round a positively-charged nucleus is one particular example of the general problem of the motion of a particle in a field of force, and for this we know that the trajectory will be controlled by the force which acts on the particle. Thus, in the absence of a field of force, a particle moves in a straight line, whilst in a uniform field (e.g. gravitational attraction) the path is a parabola. If we consider the (at first sight) quite different problem of the path of a ray of light, we see that this is controlled by the variation of the refractive index in the medium through which the light travels. Thus, in a medium of uniform refractive index, light travels in straight lines, whilst a varying refractive index results in a curved trajectory. It is found that the trajectories of a particle in a field of force, and of a ray of light in a medium of varying refractive index, can be expressed in the form of generalized equations which are mathematically similar, so that any problem of a particle in a field of force can be rewritten in the form of a problem of the trajectory of a ray of light in a medium whose refractive index varies in the appropriate way. Now, the trajectory of a ray of light can be expressed in terms of the wave theory of light, and consequently the problem of the trajectory of a particle in a field of force can be rewritten as a problem in wave theory, with the field of force playing roughly the same part as the variation of refractive index. If this is done, the interesting fact then emerges that, as long as the refractive index does not vary too greatly over the distance of a wavelength, the simple correspondence between the trajectories of a particle and a light ray persists. But if the refractive index varies appreciably over the distance of a wavelength, the wave theory indicates new effects (e.g. interference, dispersion, &c.), which cannot be interpreted in terms of the "rays" of the older geometrical optics. Consequently, if we hold fast to our correspondence between force and variation of refractive index, the transference of our mechanical problem to a problem in wave theory will lead to new effects when we deal with strong forces at small distances, as in the problem of atomic structure.