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Chapter I.—Preface 1

In this chapter, the point of view from which the whole monograph has been written is described. The monograph is intended to portray, in general terms, the principles of the electron theory of metals, so that the reader who has had no recent training in this branch of physics may appreciate the bearing of this work on metallurgy.

Chapter II.—The New Approach to Metallurgy 4

The newer theories of the metallic state are the outcome of many years of all types of research. Chapter II reviews the development of metallurgical science, by means of the microscope, the phase rule, and increasingly sensitive methods of research, to the point at which the physical theories begin to be of assistance to it. The application of X-ray methods to metallurgy was of great importance, and led to sounder classifications and co-ordinations than had previously been possible. More or less simultaneous advances in physical theory were being made, and as a result of the clues given by this work, experimental work in physical metallurgy could be planned in such a way as to produce important results and fill significant gaps in existing knowledge. Work now in progress tends to emphasize the part played by the electronic structure of metals in alloy formation, and other characteristic phenomena. It is therefore advisable for metallurgists to appreciate the principles involved, particularly because the electron theory may eventually provide the basis for a theory of metals and alloys capable not only of interpreting but also of predicting alloy properties.

Chapter III.—Some Basic Principles of Atomic Theory 10

The electron theory involves conceptions which may be somewhat unfamiliar to those who have had few recent contacts with modern physics. These conceptions, however, developed naturally from imperfections in the ideas with which most readers are already familiar, and which, for the sake of completeness and in order to provide a sound background, are discussed in this chapter. Little progress can be made in understanding the behaviour of assemblies of atoms, such as metal crystals, until the nature of the atom itself is clear. Further, the application of the ideas of modern physics to crystals is complicated, and discussion is facilitated if attention is first given to the way in which our ideas of the atom are affected. Our description, therefore, begins with the atom. The imperfection in the Rutherford theory of the atom lay in the fact that the planetary electrons could not form a stable system, but should lose their energy continuously by emitting radiation. In order to account for the marked stability of atoms, Bohr added to the Rutherford model the conceptions of the quantum theory developed by Planck. The application of the quantum theory to problems of atomic structure was a very marked advance, and led to a fuller understanding of the atom.

Chapter IV.—The Bohr Theory of the Atom 18

In this chapter the Bohr theory of the atom is further discussed. Bohr, in order to resolve the problem of the planetary electrons, made the assumption that among the infinite number of orbits which were possible in the Rutherford model, there existed a series in which an electron could rotate without emitting radiation. He further assumed that the quantum theory applied to the electron when it occupied one of these special orbits. The development of these ideas led to the recognition of the "quantization" of electrons in atoms, or grouping of the electrons of an atom into definite energy states. This allowed an exact calculation of the energy values which the electron of a hydrogen atom could possess, and the interpretation of the spectrum of hydrogen became possible, as well as other advances. The theory could, however, only be applied to the hydrogen atom, consisting of one proton and one electron.

Application to systems composed of more than two interacting bodies proved too difficult from the mathematical standpoint. Another difficulty was that quantum restrictions were arbitrarily imposed upon the energy of the electron, whose motion was otherwise treated by the laws of classical dynamics. In an effort to remove the arbitrary nature of the theory, work was carried out which greatly modified the principles involved.

Chapter V.—The Probability Conceptions 23

Before the ideas of the quantum theory could be applied to more complex atoms than that of hydrogen, or to assemblies of atoms, a new mathematical framework was required, which would allow much more general calculations to be made. Since an appreciation of the new mechanics is necessary for understanding the results which are obtained for metals, some aspects of the development of such a means of calculation are described in this chapter, and application to the hydrogen atom is discussed as a relatively simple preliminary to its application to metals. The first step towards the new theories follows from the "Uncertainty Principle" of Heisenberg, which shows that classical mechanics cannot be applied to the motion of electrons. It is theoretically impossible to specify accurately both the position and momentum of an electron at a given moment. The new theories recognize this, and concentrate on the energies of the electrons without exactly specifying their positions. This is done by following the lead of de Broglie, who showed that the behaviour of electrons in motion could be calculated by applying equations analogous to those of the wave theory of light, provided that the wavelength used bore a definite relationship to the electronic energy. The wave equation used for calculating the behaviour of electrons is discussed, in order to show that only certain definite solutions are possible, and that, in the case of the hydrogen atom, these solutions give electronic energy levels identical with those calculated on the Bohr theory. This establishes the validity of the method, and also shows that the wave equation demonstrates the existence of quantum levels without unsatisfactory assumptions. Although the results obtained by solving wave equations do not specify the position of the electron exactly, they do allow the probability of the electron being in a given position to be calculated.

Chapter VI.—Application to Metals 36

The application of wave mechanics to atoms, which was discussed in Chapter V, may be extended to assemblies of atoms. The problem is a complex one, insofar as the energy characteristics of the valency electrons are affected by the distance apart of atoms in the assemblage, and also by the relative positions of the atoms in space, that is, by the crystal structure of the solid. In this chapter, the complications introduced by considerations of crystal structure are neglected, and the general effect of bringing atoms together to form an assembly is discussed. This treatment brings out the essential nature of metals, and to the picture obtained, the effect of crystal structure may easily be added. It is shown that, in a metal, the energies of the valency electrons lie within a certain range of energy levels, which are extremely close together. Each level can be occupied by two electrons. As will be shown in later chapters, it is of importance, for the understanding of alloy formation and other metallic properties, to know how the energy levels are arranged within the permissible range. This is described in terms of the number of energy levels which occur between two slightly separated values of the energy. The picture of a metal built up in this chapter accounts qualitatively for many phenomena, such as electrical conductivity, but is not complete. Modifications need to be introduced in order to explain the differences between conductors of electricity and insulators.

Chapter VII.—The Effect of Crystal Structure 44

In order to complete the picture developed in Chapter VI, account must be taken of the effect of crystal structure, which modifies the distribution

of the electronic energy states. Only when this is done can the theory be applied quantitatively to real metals and alloys. A new way of characterizing the energies of electrons is introduced in this chapter, because it enables the quantitative application of the theory to alloy phases to be followed relatively simply. Energies are described in terms of a "wave-number," k , which is the reciprocal of the wave-length which occurs in the de Broglie equations employed to calculate the behaviour of electrons. It is shown that, when account is taken of crystal structure, the theory indicates that there exist ranges of forbidden energy which the electrons in a metal cannot possess if they are to be free to move inside the metal. Such forbidden ranges occur at critical values of k , which differ according to the direction of motion of the electron with respect to the planes of the crystal lattice. By considering, for simplicity, a hypothetical two-dimensional metal, it is shown how the electron energies may be plotted as contours inside the so-called Brillouin zones, the derivation of which is explained, while the modifying influence of the energy gaps on the form of the distribution of energy levels discussed in Chapter VI is also considered. As shown in later chapters, this modification is of the first importance in understanding the theory of alloys.

Chapter VIII.—Application to Alloy Structures 52

The derivation of the Brillouin zones for a hypothetical two-dimensional metal, discussed in the previous chapter, is extended to the case of the real three-dimensional structure by similar methods, and the forms of the zones for the face-centred cubic and body-centred cubic structures are described. By considering a gradual increase in the number of valency electrons per atom for a face-centred cubic metal such as copper, it is shown how the structure may be expected, from the form of the zone and the appropriate distribution of energy states, to become unstable at a definite ratio of electrons to atoms, which is in excellent agreement with the ratio deduced experimentally by Hume-Rothery for the maximum solid solubilities of various elements in copper and silver. Similar applications of the electron theory may be made to account for the existence of the "electron compounds" which occur at electron to atom ratios of 3 : 2, 21 : 13, and 7 : 4, respectively. The implications of the zone theory in alloy formation are discussed in general terms.

Chapter IX.—Approximations Involved in the Results of the Electron Theories 63

In this chapter reference is made to the complexity of the problem of the metallic state from the mathematician's point of view, and some of the general approximations which have to be made are indicated.

Chapter X.—Insulators and Conductors 65

The electrical conductivity of metals is due to the motion of electrons, and the mechanism by which current is carried, and resistance set up, is briefly described in this chapter. In previous chapters, the forms of Brillouin zones and the distribution of electron energy states have been discussed; it is now shown how these factors account for the differences between conducting and insulating crystals. In the case of an insulator, the valency electrons possess energies which account for all the possible energy states within a Brillouin zone, and such electrons cannot be accelerated by an applied electric field. Conductors, however, possess vacant energy states to which electrons of lower energy may be promoted. The theory also accounts qualitatively for the characteristic differences which exist between the conductivities of monovalent and polyvalent metals. The application of the theory to the electrical conductivity of alloys, however, involves many difficulties. In certain favourable cases, relative results, as opposed to absolute magnitudes, may be obtained, which are in very fair agreement with experiment.

Chapter XI.—Magnetic Properties of Metals and Alloys 73

Certain elementary principles of magnetism follow quite naturally from the picture of a metal which has been developed in earlier sections. The two electrons which have been described as able to occupy the same energy level differ only in the sense of their magnetic moments in the presence of a magnetic field. In this chapter it is shown how the band theory of metals, when the difference between the two electrons which occupy the same energy level is taken into account, enables the phenomenon of paramagnetism to be interpreted. The principles involved are extended to ferromagnetism. The criteria for ferromagnetism, which involve not only a suitable electronic structure, but also a favourable ratio of the atomic radius to the ionic radius, are discussed. The theory suggests that by a suitable choice of alloying elements, new ferromagnetic alloys might be developed. The thermal expansion of ferromagnetics is discussed in general terms, and leads to the possibility of the control of the thermal expansion of certain types of alloys.

Chapter XII.—The Cohesion of Metals 87

Previous chapters having been devoted mainly to the elucidation of the energy distribution of the valency electrons in metals, and the effect of this on various phenomena, attention is drawn in this chapter to the energy of the metallic structure as a whole. It is possible to calculate from first principles, with some accuracy, the binding energy of certain simple metallic crystals of known structure, and this measures the stability of the crystal relative to the free atoms of which it is composed. The same methods give a theoretical estimate of the lattice spacing, and enable theoretical calculations of compressibility and elastic constants to be made. The electron theory is therefore able to interpret satisfactorily the elastic properties of metals. Application to plastic deformation, however, is at present hardly possible. Certain aspects of the theory of plastic deformation, which starts from the somewhat different standpoint of faults or "dislocations" in the metal lattice, are referred to. It is possible that developments of the electron theories may eventually link up with the dislocation theory of deformation.

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