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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. 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, 58·94, 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 127·61, atomic number 52) and iodine (atomic weight 126·91, 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 an 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

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

Table I.—*International Atomic Weights*, 1957.

	Symbol.	At. No.	At. Wt.*		Symbol.	At. No.	At. Wt.*
Actinium	Ac	89	[227]	Molybdenum	Mo	42	95·95
Aluminium	Al	13	26·98	Neodymium	Nd	60	144·27
Americium	Am	95	[243]	Neon	Ne	10	20·183
Antimony	Sb	51	121·76	Neptunium	Np	93	[237]
Argon	A	18	39·944	Nickel	Ni	28	58·71
Arsenic	As	33	74·91	Niobium	Nb		
Astatine	At	85	[210]	(Columbium)	(Cb)	41	92·91
Barium	Ba	56	137·36	Nitrogen	N	7	14·008
Berkelium	Bk	97	[245]	Nobelium	No	102	—
Beryllium	Be	4	9·013	Osmium	Os	76	190·2
Bismuth	Bi	83	209·00	Oxygen	O	8	16·0000
Boron	B	5	10·82	Palladium	Pd	46	106·4
Bromine	Br	35	79·916	Phosphorus	P	15	30·975
Cadmium	Cd	48	112·41	Platinum	Pt	78	195·09
Caesium	Cs	55	132·91	Plutonium	Pu	94	[242]
Calcium	Ca	20	40·08	Polonium	Po	84	[210]
Californium	Cf	98	[248]	Potassium	K	19	39·100
Carbon	C	6	12·011	Praseodymium	Pr	59	140·92
Cerium	Ce	58	140·13	Promethium	Pm	61	[145]
Chlorine	Cl	17	35·457	Protactinium	Pa	91	[231]
Chromium	Cr	24	52·01	Radium	Ra	88	[226·05]
Cobalt	Co	27	58·94	Radon	Rn	86	[222]
Copper	Cu	29	63·54	Rhenium	Re	75	186·22
Curium	Cm	96	[245]	Rhodium	Rh	45	102·91
Dysprosium	Dy	66	162·51	Rubidium	Rb	37	85·48
Einsteinium	Es	99	—	Ruthenium	Ru	44	101·1
Erbium	Er	68	167·27	Samarium	Sm	62	150·35
Europium	Eu	63	152·0	Scandium	Sc	21	44·96
Fermium	Fm	100	—	Selenium	Se	34	78·96
Fluorine	F	9	19·00	Silicon	Si	14	28·09
Francium	Fr	87	[223]	Silver	Ag	47	107·880
Gadolinium	Gd	64	157·26	Sodium	Na	11	22·991
Gallium	Ga	31	69·72	Strontium	Sr	38	87·63
Germanium	Ge	32	72·60	Sulphur	S	16	32·066†
Gold	Au	79	197·0	Tantalum	Ta	73	180·95
Hafnium	Hf	72	178·50	Technetium	Tc	43	[99]
Helium	He	2	4·003	Tellurium	Te	52	127·61
Holmium	Ho	67	164·94	Terbium	Tb	65	158·93
Hydrogen	H	1	1·0080	Thallium	Tl	81	204·39
Indium	In	49	114·82	Thorium	Th	90	232·05
Iodine	I	53	126·91	Thulium	Tm	69	168·94
Iridium	Ir	77	192·2	Tin	Sn	50	118·70
Iron	Fe	26	55·85	Titanium	Ti	22	47·90
Krypton	Kr	36	83·80	Tungsten	W	74	183·86
Lanthanum	La	57	138·92	Uranium	U	92	238·07
Lead	Pb	82	207·21	Vanadium	V	23	50·95
Lithium	Li	3	6·940	Xenon	Xe	54	131·30
Lutecium	Lu	71	174·99	Ytterbium	Yb	70	173·04
Magnesium	Mg	12	24·32	Yttrium	Y	39	88·92
Manganese	Mn	25	54·94	Zinc	Zn	30	65·38
Mendelenium	Md	101	—	Zirconium	Zr	40	91·22
Mercury	Hg	80	200·61				

* 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. These values are not included in the International Table for 1957.

† Because of natural variations in the relative abundance of its isotopes, the atomic weight of sulphur has a range of ±0·003.

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 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.*

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* *Elementary :*
O. R. Frisch, " Meet the Atoms ". **1946** : New York (L. B. Fischer Publishing Corporation).
C. F. Powell and G. P. S. Occhialini, " Nuclear Physics in Photographs ". **1947** : Oxford (Clarendon Press).
Intermediate :
D. Halliday, " Introductory Nuclear Physics ". **1950** : New York (John Wiley and Sons, Inc.); London (Chapman and Hall, Ltd.).
F. K. Richtmyer and E. H. Kennard, " Introduction to Modern Physics ", 4th edn., Chapter XI, p. 542. **1947** : New York (McGraw-Hill Book Co., Inc.); London (McGraw-Hill Publishing Co., Ltd.).
Advanced :
H. A. Bethe, " Elementary Nuclear Theory ". **1947** : New York (John Wiley and Sons, Inc.); London (Chapman and Hall, Ltd.).
E. Fermi, " Nuclear Physics ". **1950** : Chicago (University Press); Oxford (Clarendon Press).

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 gradual 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.

The first problem of extra-nuclear atomic structure was to determine the arrangement or grouping of the electrons round 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. 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 $\frac{h}{2\pi}, \frac{2h}{2\pi}, \frac{3h}{2\pi} \ldots$ 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

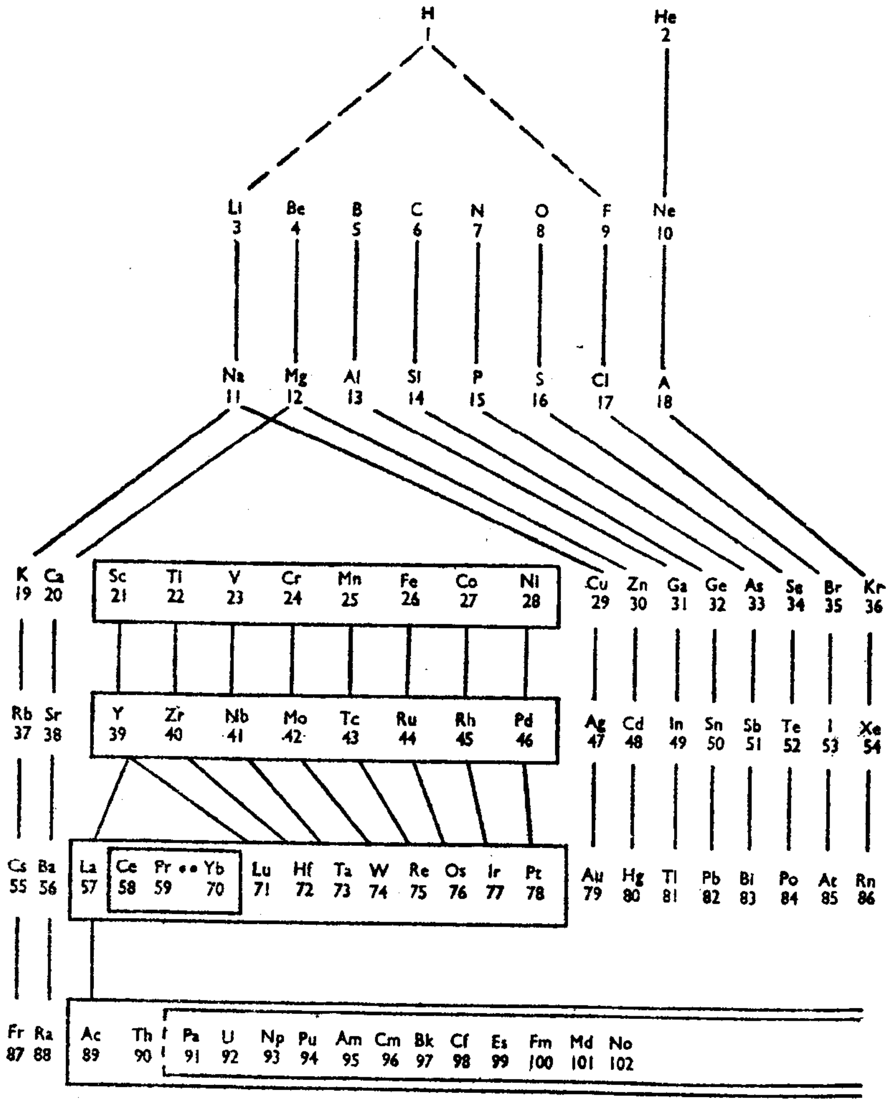

Fig. 1.—Periodic Table of the Elements.

The recently discovered trans-uranic elements form a group of so-called "actinides", analogous to the rare-earth metals in the preceding Long Period. Element 43, originally called masurium (Ma), has now been prepared by the methods of nuclear physics and renamed technetium (Tc).

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. In this way de Broglie and Schrödinger were led to suggest that the transference of a mechanical problem to a problem in wave theory might lead to a mechanics of the atom. Needless to say, this was at first regarded as little but speculation, but the whole position was changed when in 1927 Davisson and Germer, and G. P. Thomson discovered that electrons exhibited interference effects, an electron of momentum, p, acting as though it possessed a wavelength λ, given by the relation :

$$\lambda = \frac{h}{p}$$

where h is the Planck's constant of specific-heat theory and equals $6{\cdot}624 \times 10^{-27}$ erg-sec. For a velocity, u, which is small compared with that of light, the above relation reduces to :

$$\lambda = \frac{h}{mu}$$

This discovery showed that electrons were somehow associated with wave-like characteristics, and that the mathematical speculations had revealed a real characteristic of matter. It is important to realize that wave mechanics came into existence as the result of pure mathematical reasoning, before there was any evidence for the wave-like properties of an electron.

As explained above, wave mechanics came into being by transferring a mechanical problem into a problem of wave theory, and when this is done the resulting equations naturally contain terms which, if the problem were really one of physical waves, would represent wavelengths, frequencies, &c. This, however, does not mean that the hypothetical waves have any real physical existence—they are purely imaginative quantities which arise from the mathematical correspondence. Some people find great difficulty in accepting this, and the following analogy may help to show how the equations for the motion of an electron may be of a wave-like nature, without the electron itself being a wave.

If a rod of steel is held in torsion, there is a certain mathematical equation expressing the torsional stress as a function of the properties of the material, external shape, &c. This equation can be solved in simple, but not in complicated, cases. If a soap-bubble is blown from a tube, its curvature is determined by the properties of the soap film, the shape of the orifice, &c., and can be expressed by a mathematical equation. It was shown by G. I. Taylor * that the two mathematical equations were of the same form, and resembled each other so completely that, when the equation for torsional stress could not be solved, it was possible to blow the appropriate soap-bubble (or a rubber membrane) and then, from measurements of its curvature, to deduce the solution to the problem in torsional stress. In this way we may say that a problem of stress has been converted into one of soap-bubble curvature, but this is a purely mathematical correspondence, and does not imply that torsional stress is the same thing as the curvature of a soap-bubble. In the same way, the fact that the problem of the motion of an electron can be expressed in the equations of a wave theory does not imply that the electron is a wave.

The wave mechanics indicates that it is no longer permissible to think of an electron as describing an orbit. All that can be stated is the probability that an electron will be found in a given region of the atom, and this probability is represented by a certain wave function, the square of whose amplitude at a given place is a measure of the probability of finding an electron at the place concerned. Thus, in an electron-diffraction experiment, the directions of the diffracted rays are those for which the amplitude of the wave equation is greatest. Wave mechanics provides us with the appropriate mathematical method of calculating these probabilities, and the electron is moving so rapidly that for many purposes it is justifiable to regard an atom as consisting of a minute nucleus of charge $+Ze$, surrounded by a cloud of negative electricity, whose density at any one place is proportional to the probability of finding an electron at this particular place; the total negative charge is equal to $-Ze$, so that the atom as a whole is electrically neutral. In the lowest state of the hydrogen atom, for example, the electron cloud is spherically symmetrical, in contrast to the older orbital theory where the electron was confined to one plane. The cloud is most dense at the centre of the atom, and is of negligible density at distances greater than about 2 Å. from the nucleus. This means that there is a negligible probability of finding an electron at a distance greater than about 2 Å. from the nucleus, and that, within this distance, the probability of finding the electron in an element of space becomes greater as the nucleus is approached. These electron clouds

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* See R. V. Southwell: "An Introduction to the Theory of Elasticity for Engineers and Physicists", p. 357. 1936: Oxford (Clarendon Press).

are the best "pictures" which can be obtained of the structure of an atom, and it is not possible to say anything about the motion of the electrons inside the electron cloud characteristic of the stationary state of an atom. According to the Uncertainty Principle of Heisenberg,* it is meaningless to speak of the motion of an electron within a stationary state, because the mere concept of motion implies that the electron can be observed more than once in the same stationary state. Actually, the first observation on the electron will disturb its motion slightly, because an observation cannot be made without some interaction with the outside world, and this interaction must cause a slight disturbance of the thing observed, and so prevent a second measurement of the same stationary state. The wave mechanics provides exactly what is wanted by the Heisenberg Principle,* and we have to accept the fact that, on the atomic scale, we cannot follow the electron in detail along its trajectory, but can only describe it in terms of probabilities.

Although the electron-cloud picture of an atom is in terms of probabilities, and not of precise orbits, the energy associated with a stationary state of an atom is exact. Just as a vibrating string can give rise to stationary vibrations only if the wavelengths are related by whole numbers to the length of the string, so the wave equation for the motion of an electron round an atom can give rise to a stationary state only if whole numbers are introduced, and it is found that a complete description of a stationary state involves the introduction of four whole numbers, or quantum numbers, which are denoted n, l, m_l, and m_s. Of these n is numerically equal to the n of the Bohr theory, and for the hydrogen atom the negative energy is inversely proportional to n^2. Just as the orbits of the Bohr theory became larger with increasing n, so the extent of the electron cloud increases with n. Thus, for the hydrogen atom in the state for which $n = 2$, the electron cloud is larger than that for the state for which $n = 1$. In each case, however, there is only one electron, and consequently the electron cloud is on the whole more diffuse in the state for which $n = 2$, since in each case the probability of finding the electron somewhere in the region of the whole cloud must equal unity.

The second quantum number l is numerically equal to $(k - 1)$ of the Bohr theory, and is again a measure of the angular momentum associated with the motion of the electron; this is usually referred to as the *orbital angular momentum*, although the retention of the term "orbital"

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* For a description of the Heisenberg Principle, the following books may be consulted: J. I. Frenkel, " Wave Mechanics: Elementary Theory ". **1932** : Oxford (Clarendon Press). W. Hume-Rothery, " Atomic Theory for Students of Metallurgy ", (*Inst. Metals Monograph and Rep. Series*, No. 3), 3rd revised edition. **1960** : London.

is unfortunate, since we must no longer visualize an orbit. For a hydrogen-like atom the orbital angular momentum is of magnitude $\frac{h}{2\pi}\sqrt{l(l+1)}$, so that Bohr's postulate of an integral multiple of $\frac{h}{2\pi}$ was not quite correct. l may have any value from 0 to $(n-1)$, but a state for which $l = 0$ is not to be regarded as one for which the electron is at rest, but rather as one in which the motion is as likely to be in one direction as another, and so does not give rise to a resultant angular momentum.

The third quantum number m_l may have any value from $-l$ to $+l$, and is a measure of the component of the orbital angular momentum about some specified axis, which is defined as the direction of a superimposed weak magnetic field. The orbital angular momentum $\frac{h}{2\pi}\sqrt{l(l+1)}$ is associated with a magnetic moment of magnitude $\frac{eh}{4\pi mc}\sqrt{l(l+1)}$, where m is the mass of the electron, and c is the velocity of light. The component of this magnetic moment in the direction of a weak magnetic field is $\frac{eh}{4\pi mc}\cdot m_l$, where the quantity $\frac{eh}{4\pi mc}$ is known as a *Bohr Magneton*, and is equal to $0{\cdot}9 \times 10^{-20}$ erg.gauss^{-1}. Electrons in states with the same values of n and l, and with different values of m_l, have the same energy in the absence of a magnetic field, and are said to be *degenerate*. In the presence of a magnetic field, the degeneracy is removed, and for a given n and l, the different values of m_l give rise to slightly different energies. This is shown by the *Zeeman Effect*, in which the application of a magnetic field causes a splitting of spectral lines.

The fourth quantum number m_s refers to the spin of an electron, which gives rise to a magnetic moment of magnitude $\frac{eh}{2\pi mc}\sqrt{s(s+1)}$, where $s = \frac{1}{2}$, and the component of this in the direction of an applied magnetic field is equal to $\frac{eh}{2\pi mc}\cdot m_s$, where $m_s = \pm\frac{1}{2}$, so that the component in the direction of the field is equal to $\pm\frac{eh}{4\pi mc} = \pm 1$ Bohr magneton.

In a hydrogen-like atom, an electronic state is thus defined by specifying the four quantum numbers n, l, m_l, and m_s. For brevity, electrons in states for which $l = 0$, 1, 2, and 3 are referred to as s, p, d, and f electrons, respectively, and it is customary to denote the value of n by a figure preceding the letter which denotes the value of l. Thus, an electron in a state for which $n = 3$, $l = 1$ is called a $3p$ electron. Each electron state has a definite energy, and a characteristic electron-cloud pattern; examples of these for s, p, and d states are given in Hume-Rothery's " Atomic Theory for Students of Metallurgy ".

For atoms containing more than one electron, the problem is enormously more complicated, because each electron moves in the field, not merely of the nucleus, but of all the other electrons. As an approximation, an electron state may still be described by the four quantum numbers n, l, m_l, and m_s, and the symbols s, p, d, and f are again used as abbreviations for $l = 0, 1, 2, 3$, respectively. A small superscript numeral outside a bracket is used to denote the number of electrons in the state concerned. Thus, the lowest energy state of the atom of boron may be written $(1s)^2(2s)^2(2p)^1$, and this means that the atom contains two electrons in the $(1s)$ state, two in the $(2s)$ state, and one in the $(2p)$ state.

The electron clouds of s-states are spherically symmetrical, and contain $(n - 1)$ spherical nodes.* The clouds of p-states have a node at the centre, and $(n - 2)$ spherical nodes, and their directional characteristics are as shown in Fig. 5, (p. 22), whilst those of d-states contain a node at the centre and $(n - 3)$ spherical nodes, and have more complicated shapes. Complete sub-groups of $(np)^6$, $(nd)^{10}$, or $(nf)^{14}$ electrons possess electron clouds which, in the simplest state, are spherically symmetrical, but whose slopes cannot yet be calculated accurately.

It might at first be thought that the lowest energy of an atom would result from placing all the electrons in the lowest, or $1s$ state. Actually this is not so, and the facts are summarized by the *Pauli Exclusion Principle*, according to which no two electrons can be in exactly the same state as defined by all four quantum numbers. We may, for example, have one electron in the state characterized by the quantum numbers ($4, 3, 2$, and $+\frac{1}{2}$), and another in the state ($4, 3, 2, -\frac{1}{2}$), but we cannot have two electrons in a ($4, 3, 2, +\frac{1}{2}$) state. Since the quantum number m_s is always $\pm\frac{1}{2}$, the Principle is sometimes expressed by saying that a given electron state can contain not more than two electrons, which must be of opposite spin.

The Pauli Principle was first put forward empirically, but was readily incorporated into wave mechanics by making an appropriate assumption about the form of the wave functions. It is of great importance, because, by placing a limit on the number of electrons in a given state, it leads to the concept of groups and sub-groups of electrons,

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* A node is a region where the amplitude of a vibration is zero, and so a node in an electron cloud means a region where the probability of finding an electron is zero.

and this is what is needed to explain a periodic repetition of properties. For the present understanding of alloy structures it is necessary to consider only the first two quantum numbers *n* and *l*, and Table II gives the accepted electronic structures for the free atoms of the elements in their lowest energy states.

This table shows clearly how the regular sequence is due to the building up of groups or shells of electrons. The groups of 2 electrons in the 1-quantum shell, and of 8 electrons in the 2-quantum shell, when once they are complete, remain as stable groups which persist unchanged in all the later elements; but in the electron shells of higher quantum number, the groups of 8 electrons have a provisional stability only, and later expand into groups of 18 electrons, by the building up of a sub-group of ten *d*-electrons. The process in which a group of 8 electrons expands into one of 18 takes place in the so-called *transition elements* of the Long Periods. Pauli's Principle means that the maximum number of electrons in a shell of principal quantum number *n* is equal to $2n^2$. Consequently, the group of 18 electrons is the maximum which can exist in the 3-quantum shell, but in the 4-quantum shell there is the possibility of a further expansion to a complete group of 32, by the building up of a sub-group of fourteen (4*f*) electrons. Table II shows that this process takes place in the group of elements known as the *Rare Earths*, or *lanthanides*, or *lanthanons*, which occur in the middle of the transition elements of the Third Long Period. It is now recognized that the newly discovered trans-uranic elements occur at the position in the Periodic Table where the 5-quantum group of 18 electrons is expanding into one of 32 by the building up of the (5*f*) sub-group of 14 electrons, and they are therefore called *actinides* to emphasize their resemblance to the lanthanides.

It is important to note that the 8 electrons in a group are not exactly equivalent, but fall into the sub-groups of 2 and 6 electrons, respectively. The formation of this sub-group of 2 electrons is of great importance in metallurgy, since in some cases the stability of the sub-group is so great that it persists in the solid crystal. Thus, thallium has three valency electrons in the 6-quantum shell, two of these being in the sub-group for which ($n = 6, l = 0$), and one in the sub-group ($n = 6, l = 1$). In the crystal of metallic thallium it is fairly certain that the sub-group of 2 electrons persists unchanged, so that although thallium has three valency electrons per atom, it is essentially a univalent metal in the solid crystal (see p. 55). This, of course, is quite in accordance with the facts of chemistry, which indicate that the univalent thallous salts are very stable. It must be emphasized that the electronic structures in Table II refer to free atoms, and that in liquid or solid metals the

TABLE II.—*Atomic Structures* (1).

Element and Atomic Number.	Principal and Secondary Quantum Numbers.									
$n =$	1	2		3			4			
$l =$	0	0	1	0	1	2	0	1	2	3
1 H	1									
2 He	2									
3 Li	2	1								
4 Be	2	2								
5 B	2	2	1							
6 C	2	2	2							
7 N	2	2	3							
8 O	2	2	4							
9 F	2	2	5							
10 Ne	2	2	6							
11 Na	2	2	6	1						
12 Mg	2	2	6	2						
13 Al	2	2	6	2	1					
14 Si	2	2	6	2	2					
15 P	2	2	6	2	3					
16 S	2	2	6	2	4					
17 Cl	2	2	6	2	5					
18 A	2	2	6	2	6					
19 K	2	2	6	2	6		1			
20 Ca	2	2	6	2	6		2			
21 Sc	2	2	6	2	6	1	2			
22 Ti	2	2	6	2	6	2	2			
23 V	2	2	6	2	6	3	2			
24 Cr	2	2	6	2	6	5	1			
25 Mn	2	2	6	2	6	5	2			
26 Fe	2	2	6	2	6	6	2			
27 Co	2	2	6	2	6	7	2			
28 Ni	2	2	6	2	6	8	2			
29 Cu	2	2	6	2	6	10	1			
30 Zn	2	2	6	2	6	10	2			
31 Ga	2	2	6	2	6	10	2	1		
32 Ge	2	2	6	2	6	10	2	2		
33 As	2	2	6	2	6	10	2	3		
34 Se	2	2	6	2	6	10	2	4		
35 Br	2	2	6	2	6	10	2	5		
36 Kr	2	2	6	2	6	10	2	6		

distribution of the electrons in the outermost groups is not necessarily the same. Thus, the free atom of nickel has two electrons in the 4-quantum shell, and sixteen electrons in the 3-quantum shell; but in solid nickel there is on the average only 0·6 electron per atom in states derived from

TABLE II (*contd.*).—*Atomic Structures* (2).

Element and Atomic Number.	Principal and Secondary Quantum Numbers.										
n =	1	2	3	4				5			6
l =	—	—	—	0	1	2	3	0	1	2	0
37 Rb .	2	8	18	2	6			1			
38 Sr .	2	8	18	2	6			2			
39 Y .	2	8	18	2	6	1		2			
40 Zr .	2	8	18	2	6	2		2			
41 Nb .	2	8	18	2	6	4		1			
42 Mo .	2	8	18	2	6	5		1			
43 Tc .	2	8	18	2	6	6		1			
44 Ru .	2	8	18	2	6	7		1			
45 Rh .	2	8	18	2	6	8		1			
46 Pd .	2	8	18	2	6	10		—			
47 Ag .	2	8	18	2	6	10		1			
48 Cd .	2	8	18	2	6	10		2			
49 In .	2	8	18	2	6	10		2	1		
50 Sn .	2	8	18	2	6	10		2	2		
51 Sb .	2	8	18	2	6	10		2	3		
52 Te .	2	8	18	2	6	10		2	4		
53 I .	2	8	18	2	6	10		2	5		
54 Xe .	2	8	18	2	6	10		2	6		
55 Cs .	2	8	18	2	6	10		2	6		1
56 Ba .	2	8	18	2	6	10		2	6		2
57 La .	2	8	18	2	6	10		2	6	1	2
58 Ce .	2	8	18	2	6	10	2	2	6		2
59 Pr .	2	8	18	2	6	10	3	2	6		2
60 Nd .	2	8	18	2	6	10	4	2	6		2
61 Pm .	2	8	18	2	6	10	5	2	6		2
62 Sm .	2	8	18	2	6	10	6	2	6		2
63 Eu .	2	8	18	2	6	10	7	2	6		2
64 Gd .	2	8	18	2	6	10	7	2	6	1	2
65 Tb .	2	8	18	2	6	10	9	2	6		2
66 Dy .	2	8	18	2	6	10	10	2	6		2
67 Ho .	2	8	18	2	6	10	11	2	6		2
68 Er .	2	8	18	2	6	10	12	2	6		2
69 Tm .	2	8	18	2	6	10	13	2	6		2
70 Yb .	2	8	18	2	6	10	14	2	6		2
71 Lu .	2	8	18	2	6	10	14	2	6	1	2
72 Hf .	2	8	18	2	6	10	14	2	6	2	2

the (4*s*) state of the free atom, and 17·4 electrons per atom in states derived from those of the 3-quantum shell. Similarly, in magnesium the two valency electrons form the complete (3*s*) sub-group in the free atom, but in the solid metal a fraction of the valency electrons is in states derived from the (3*p*) sub-group. In some metallurgical papers