

NOBEL LECTURES

PHYSICS



1922 – 1941

World Scientific

NOBEL LECTURES IN PHYSICS
1922-1941

NOBEL LECTURES
INCLUDING PRESENTATION SPEECHES
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INCLUDING PRESENTATION SPEECHES
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Foreword

Since 1901 the Nobel Foundation has published annually “Les Prix Nobel” with reports from the Nobel Award Ceremonies in Stockholm and Oslo as well as the biographies and Nobel lectures of the laureates. In order to make the lectures available to people with special interests in the different prize fields the Foundation gave Elsevier Publishing Company the right to publish in English the lectures for 1901-1970, which were published in 1964-1972 through the following volumes:

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Elsevier decided later not to continue the Nobel project. It is therefore with great satisfaction that the Nobel Foundation has given World Scientific Publishing Company the right to bring the series up to date.

The Nobel Foundation is very pleased that the intellectual and spiritual message to the world laid down in the laureates' lectures will, thanks to the efforts of World Scientific, reach new readers all over the world.

Lars Gyllensten
Chairman of the Board

Stig Ramel
Executive Director

Stockholm, June 1991

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Physics 1922

N I E L S B O H R

*«for his services in the investigation of the structure of atoms, and of the
radiation emanating from them »*

Physics 1922

*Presentation Speech by Professor S.A. Arrhenius, Chairman of the Nobel
Committee for Physics of the Royal Swedish Academy of Sciences*

Your Majesty, Your Royal Highnesses, Ladies and Gentlemen.

Ever since Kirchhoff and Bunsen (1860) introduced spectral analysis, that extremely important aid to investigation has produced the finest results. To begin with, material was collected and spectra were investigated not only from terrestrial objects but also from the heavenly bodies. There was a splendid harvest. Then came the second stage of research. Attempts were made to find regularities in the structure of the spectra. To begin with, it was natural to try to compare the different spectral lines which are emitted by a glowing gas with the different notes that could be produced by a vibrating solid. The vibrating bodies in a glowing gas would in that case be its atoms and molecules. But little progress could be made on this track. It was necessary to fall back on another method, namely to try by calculation to establish the connection between the various vibrations which could be emitted by a gas. Hydrogen ought to be the simplest of all gases. The Swiss Balmer in 1885 found a simple formula for the connection mentioned between the lines of hydrogen as then known. There followed a large number of investigators, such as Kayser and Runge, Ritz, Deslandres, and especially our compatriot Rydberg, who sought for similar regularities in the spectra of the other chemical elements. Rydberg succeeded in representing their light vibrations by means of formulae which exhibited a certain resemblance to Balmer's formula. These formulae contain a constant which has afterwards acquired extremely great importance and has been recorded amongst the universal and fundamental values of physics under the name of the Rydberg constant.

Now, if it were possible to obtain an idea of the structure of the atom, of course, that would form a good starting-point to create a conception of the possible light vibrations that can be emitted by an atom of hydrogen. Rutherford, who has to such an extraordinary degree wrung their secrets from the atoms, had constructed such «atom models». According to his conception, the atom of hydrogen should consist of a positive nucleus, with a unit charge, of extremely small dimensions, and about this a negatively

charged electron should describe an orbit. As probably only electric forces are at work between the nucleus and the electron, and as these electric forces follow the same law as the attraction of gravity between two masses, the path of the electron ought to be elliptical or circular, and the nucleus to be situated either in one of the foci of the ellipse or in the centre of the circle. The nucleus would be comparable to the sun and the electron to a planet. In accordance with the classical theory of Maxwell, therefore, these orbit movements should emit rays and consequently cause a loss of energy, and the electron would describe smaller and smaller tracks with a declining period of revolution and finally rush in towards the positive nucleus. Thus the track would be a spiral, and the rays of light emitted, which will require a steadily declining period of vibration, would correspond to a continuous spectrum, which, of course, is characteristic of a glowing solid or liquid body, but not at all of a glowing gas. Consequently, either the atom model must be false, or else the classical theory of Maxwell must be incorrect in this case. Ten years or so previously there would have been no hesitation in the choice between these alternatives, but the atom model would have been declared to be inapplicable. But in 1913, when Bohr began to work at this problem, the great physicist Planck of Berlin had traced his law of radiation, which could be explained only on the assumption, which was in conflict with all preceding notions, that the energy of heat is given off in the form of ((quanta)), that is to say small portions of heat, just as matter consists of small portions, i.e. the atoms. With the help of this assumption Planck succeeded, in complete accordance with experience, in calculating the distribution of energy in radiation from a hypothetically completely black body. Afterwards (in 1905 and 1907) Einstein had perfected the quantum theory and deduced therefrom several laws, such as the diminution of the specific heat of solid bodies with declining temperature and the photoelectric effect, for which discovery he has this day been awarded the Nobel Prize.

Accordingly, Bohr had no need to hesitate in his choice: he assumed that Maxwell's theory does not hold good in the present case, but that the atom model of Rutherford is correct. Thus the electrons do not emit light when they move in their tracks round the positive nucleus, tracks which we begin by assuming to be circular. The emission of light would take place when the electron jumps from one track to another. The quantity of energy which is thus radiated is a quantum. As, according to Planck, the quantum of energy is the product of the number of light vibrations with the Planckian constant, which is denoted by the letter h , it is possible to calculate the num-

ber of vibrations which corresponds to a given passing from one orbit to another. The regularity which Balmer found for the spectrum of hydrogen requires that the radii of the different orbits should be proportional to the squares of the whole numbers, that is to say as 1 to 4 to 9, and so on. And indeed Bohr succeeded, in his first treatise on this question, in calculating the Rydberg constant from other known magnitudes, namely the weight of an atom of hydrogen, the Planckian constant, and the value of the electric unit of charge. The difference between the value found by observation and the calculated value of the Rydberg constant amounted to only 1 percent; and this has been diminished by more recent measurements.

This circumstance at once attracted the admiring attention of the scientific world to Bohr's work and made it possible to foresee that he would to a great extent solve the problem before him. Sommerfeld showed that what is known as the fine structure of the hydrogen lines, by which is meant that the lines observed with a strongly dispergent spectroscope are divided up into several closely adjacent lines, can be explained in accordance with Bohr's theory in the following way. The various stationary tracks for the movement of the electrons - if we leave out of account the innermost one, which is the ordinary one, and is called the ((orbit of rest)) - may be not only circular but also elliptical, with a major axis equal to the diameter of the corresponding circular orbit. When an electron passes from an elliptical orbit to another track, the change in the energy, and consequently the number of vibrations for the corresponding spectral lines, is somewhat different from what it is when it passes from the corresponding circular orbit to the other track. Consequently we get two different spectral lines, which nevertheless lie very close to one another. Yet we observe only a smaller number of lines than we should expect according to this view of things.

The difficulties thus revealed, however, Bohr succeeded in removing by the introduction of what is known as the principle of correspondence, which opened up entirely new prospects of great importance. This principle to some extent brings the new theory nearer to the old classical theory. According to this principle, a certain number of transitions are impossible. The principle in question is of great importance in the determination of the tracks of electrons which are possible within atoms that are heavier than the atom of hydrogen. The nuclear charge of the atom of helium is twice as great as that of the atom of hydrogen: in a neutral condition it is encircled by two electrons. It is the lightest atom next that of hydrogen. It occurs in two different modifications: one is called parhelium, and is the more stable, and

NIELS BOHR

The structure of the atom

Nobel Lecture, December 11, 1922

Ladies and Gentlemen. Today, as a consequence of the great honour the Swedish Academy of Sciences has done me in awarding me this year's Nobel Prize for Physics for my work on the structure of the atom, it is my duty to give an account of the results of this work and I think that I shall be acting in accordance with the traditions of the Nobel Foundation if I give this report in the form of a survey of the development which has taken place in the last few years within the field of physics to which this work belongs.

The general picture of the atom

The present state of atomic theory is characterized by the fact that we not only believe the existence of atoms to be proved beyond a doubt, but also we even believe that we have an intimate knowledge of the constituents of the individual atoms. I cannot on this occasion give a survey of the scientific developments that have led to this result; I will only recall the discovery of the electron towards the close of the last century, which furnished the direct verification and led to a conclusive formulation of the conception of the atomic nature of electricity which had evolved since the discovery by Faraday of the fundamental laws of electrolysis and Berzelius's electrochemical theory, and had its greatest triumph in the electrolytic dissociation theory of Arrhenius. This discovery of the electron and elucidation of its properties was the result of the work of a large number of investigators, among whom Lenard and J. J. Thomson may be particularly mentioned. The latter especially has made very important contributions to our subject by his ingenious attempts to develop ideas about atomic constitution on the basis of the electron theory. The present state of our knowledge of the elements of atomic structure was reached, however, by the discovery of the atomic nucleus, which we owe to Rutherford, whose work on the radioactive substances discovered towards the close of the last century has much enriched physical and chemical science.

According to our present conceptions, an atom of an element is built up of a nucleus that has a positive electrical charge and is the seat of by far the greatest part of the atomic mass, together with a number of electrons, all having the same negative charge and mass, which move at distances from the nucleus that are very great compared to the dimensions of the nucleus or of the electrons themselves. In this picture we at once see a striking resemblance to a planetary system, such as we have in our own solar system. Just as the simplicity of the laws that govern the motions of the solar system is intimately connected with the circumstance that the dimensions of the moving bodies are small in relation to the orbits, so the corresponding relations in atomic structure provide us with an explanation of an essential feature of natural phenomena in so far as these depend on the properties of the elements. It makes clear at once that these properties can be divided into two sharply distinguished classes.

To the first class belong most of the ordinary physical and chemical properties of substances, such as their state of aggregation, colour, and chemical reactivity. These properties depend on the motion of the electron system and the way in which this motion changes under the influence of different external actions. On account of the large mass of the nucleus relative to that of the electrons and its smallness in comparison to the electron orbits, the electronic motion will depend only to a very small extent on the nuclear mass, and will be determined to a close approximation solely by the total electrical charge of the nucleus. Especially the inner structure of the nucleus and the way in which the charges and masses are distributed among its separate particles will have a vanishingly small influence on the motion of the electron system surrounding the nucleus. On the other hand, the structure of the nucleus will be responsible for the second class of properties that are shown in the radioactivity of substances. In the radioactive processes we meet with an explosion of the nucleus, whereby positive or negative particles, the so-called α - and β -particles, are expelled with very great velocities.

Our conceptions of atomic structure afford us, therefore, an immediate explanation of the complete lack of interdependence between the two classes of properties, which is most strikingly shown in the existence of substances which have to an extraordinarily close approximation the same ordinary physical and chemical properties, even though the atomic weights are not the same, and the radioactive properties are completely different. Such substances, of the existence of which the first evidence was found in the work of Soddy and other investigators on the chemical properties of the radioactive

elements, are called isotopes, with reference to the classification of the elements according to ordinary physical and chemical properties. It is not necessary for me to state here how it has been shown in recent years that isotopes are found not only among the radioactive elements, but also among ordinary stable elements; in fact, a large number of the latter that were previously supposed simple have been shown by Aston's well-known investigations to consist of a mixture of isotopes with different atomic weights.

The question of the inner structure of the nucleus is still but little understood, although a method of attack is afforded by Rutherford's experiments on the disintegration of atomic nuclei by bombardment with α -particles. Indeed, these experiments may be said to open up a new epoch in natural philosophy in that for the first time the artificial transformation of one element into another has been accomplished. In what follows, however, we shall confine ourselves to a consideration of the ordinary physical and chemical properties of the elements and the attempts which have been made to explain them on the basis of the concepts just outlined.

It is well known that the elements can be arranged as regards their ordinary physical and chemical properties in a *natural system* which displays most suggestively the peculiar relationships between the different elements. It was recognized for the first time by Mendeleev and Lothar Meyer that when the elements are arranged in an order which is practically that of their atomic weights, their chemical and physical properties show a pronounced periodicity. A diagrammatic representation of this so-called Periodic Table is given

1, where, however, the elements are not arranged in the ordinary way but in a somewhat modified form of a table first given by Julius Thomsen, who has also made important contributions to science in this domain. In the figure the elements are denoted by their usual chemical symbols, and the different vertical columns indicate the so-called periods. The elements in successive columns which possess homologous chemical and physical properties are connected with lines. The meaning of the square brackets around certain series of elements in the later periods, the properties of which exhibit typical deviations from the simple periodicity in the first periods, will be discussed later.

In the development of the theory of atomic structure the characteristic features of the natural system have found a surprisingly simple interpretation. Thus we are led to assume that the ordinal number of an element in the Periodic Table, the so-called atomic number, is just equal to the number of electrons which move about the nucleus in the neutral atom. In an imperfect

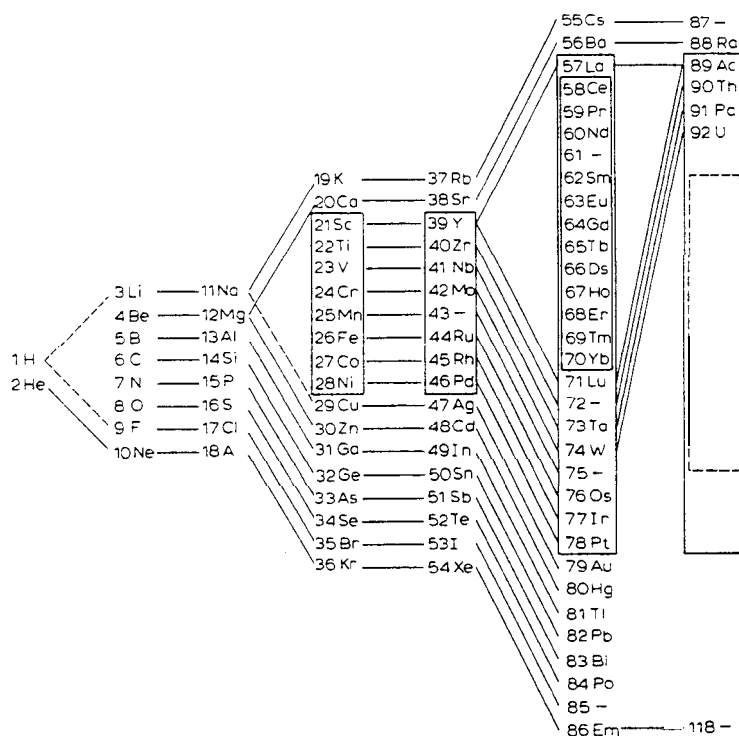


Fig. 1.

form, this law was first stated by Van den Broek; it was, however, foreshadowed by J. J. Thomson's investigations of the number of electrons in the atom, as well as by Rutherford's measurements of the charge on the atomic nucleus. As we shall see, convincing support for this law has since been obtained in various ways, especially by Moseley's famous investigations of the X-ray spectra of the elements. We may perhaps also point out, how the simple connexion between atomic number and nuclear charge offers an explanation of the laws governing the changes in chemical properties of the elements after expulsion of α - or p-particles, which found a simple formulation in the so-called radioactive displacement law.

Atomic stability ad electrodynamic theory

As soon as we try to trace a more intimate connexion between the properties of the elements and atomic structure, we encounter profound difficulties, in

that essential differences between an atom and a planetary system show themselves here in spite of the analogy we have mentioned.

The motions of the bodies in a planetary system, even though they obey the general law of gravitation, will not be completely determined by this law alone, but will depend largely on the previous history of the system. Thus the length of the year is not determined by the masses of the sun and the earth alone, but depends also on the conditions that existed during the formation of the solar system, of which we have very little knowledge. Should a sufficiently large foreign body some day traverse our solar system, we might among other effects expect that from that day the length of the year would be different from its present value.

It is quite otherwise in the case of atoms. The definite and unchangeable properties of the elements demand that the state of an atom cannot undergo permanent changes due to external actions. As soon as the atom is left to itself again, its constituent particles must arrange their motions in a manner which is completely determined by the electric charges and masses of the particles. We have the most convincing evidence of this in spectra, that is, in the properties of the radiation emitted from substances in certain circumstances, which can be studied with such great precision. It is well known that the wavelengths of the spectral lines of a substance, which can in many cases be measured with an accuracy of more than one part in a million, are, in the same external circumstances, always exactly the same within the limit of error of the measurements, and quite independent of the previous treatment of this substance. It is just to this circumstance that we owe the great importance of spectral analysis, which has been such an invaluable aid to the chemist in the search for new elements, and has also shown us that even on the most distant bodies of the 'universe there occur elements with exactly the same properties as on the earth.

On the basis of our picture of the constitution of the atom it is thus impossible, so long as we restrict ourselves to the ordinary mechanical laws, to account for the characteristic atomic stability which is required for an explanation of the properties of the elements.

The situation is by no means improved if we also rake into consideration the well-known electrodynamic laws which Maxwell succeeded in formulating on the basis of the great discoveries of Oersted and Faraday in the first half of the last century. Maxwell's theory has not only shown itself able to account for the already known electric and magnetic phenomena in all their details, but has also celebrated its greatest triumph in the prediction of the

electromagnetic waves which were discovered by Hertz, and are now so extensively used in wireless telegraphy.

For a time it seemed as though this theory would also be able to furnish a basis for an explanation of the details of the properties of the elements, after it had been developed, chiefly by Lorentz and Larmor, into a form consistent with the atomistic conception of electricity. I need only remind you of the great interest that was aroused when Lorentz, shortly after the discovery by Zeeman of the characteristic changes that spectral lines undergo when the emitting substance is brought into a magnetic field, could give a natural and simple explanation of the main features of the phenomenon. Lorentz assumed that the radiation which we observe in a spectral line is sent out from an electron executing simple harmonic vibrations about a position of equilibrium, in precisely the same manner as the electromagnetic waves in radiotelegraphy are sent out by the electric oscillations in the antenna. He also pointed out how the alteration observed by Zeeman in the spectral lines corresponded exactly to the alteration in the motion of the vibrating electron which one would expect to be produced by the magnetic field.

It was, however, impossible on this basis to give a closer explanation of the spectra of the elements, or even of the general type of the laws holding with great exactness for the wavelengths of lines in these spectra, which had been established by Balmer, Rydberg, and Ritz. After we obtained details as to the constitution of the atom, this difficulty became still more manifest; in fact, so long as we confine ourselves to the classical electrodynamic theory we cannot even understand why we obtain spectra consisting of sharp lines at all. This theory can even be said to be incompatible with the assumption of the existence of atoms possessing the structure we have described, in that the motions of the electrons would claim a continuous radiation of energy from the atom, which would cease only when the electrons had fallen into the nucleus.

The origin of the quantum theory

It has, however, been possible to avoid the various difficulties of the electrodynamic theory by introducing concepts borrowed from the so-called quantum theory, which marks a complete departure from the ideas that have hitherto been used for the explanation of natural phenomena. This theory was originated by Planck, in the year 1900, in his investigations on the law

of heat radiation, which, because of its independence of the individual properties of substances, lent itself peculiarly well to a test of the applicability of the laws of classical physics to atomic processes.

Planck considered the equilibrium of radiation between a number of systems with the same properties as those on which Lorentz had based his theory of the Zeeman effect, but he could now show not only that classical physics could not account for the phenomena of heat radiation, but also that a complete agreement with the experimental law could be obtained if - in pronounced contradiction to classical theory - it were assumed that the energy of the vibrating electrons could not change continuously, but only in such a way that the energy of the system always remained equal to a whole number of so-called energy-quanta. The magnitude of this quantum was found to be proportional to the frequency of oscillation of the particle, which, in accordance with classical concepts, was supposed to be also the frequency of the emitted radiation. The proportionality factor had to be regarded as a new universal constant, since termed Planck's constant, similar to the velocity of light, and the charge and mass of the electron.

Planck's surprising result stood at first completely isolated in natural science, but with Einstein's significant contributions to this subject a few years after, a great variety of applications was found. In the first place, Einstein pointed out that the condition limiting the amount of vibrational energy of the particles could be tested by investigation of the specific heat of crystalline bodies, since in the case of these we have to do with similar vibrations, not of a single electron, but of whole atoms about positions of equilibrium in the crystal lattice. Einstein was able to show that the experiment confirmed Planck's theory, and through the work of later investigators this agreement has proved quite complete. Furthermore, Einstein emphasized another consequence of Planck's results, namely, that radiant energy could only be emitted or absorbed by the oscillating particle in so-called «quanta of radiation»), the magnitude of each of which was equal to Planck's constant multiplied by the frequency.

In his attempts to give an interpretation of this result, Einstein was led to the formulation of the so-called « hypothesis of light-quanta », according to which the radiant energy, in contradiction to Maxwell's electromagnetic theory of light, would not be propagated as electromagnetic waves, but rather as concrete light atoms, each with an energy equal to that of a quantum of radiation. This concept led Einstein to his well-known theory of the photoelectric effect. This phenomenon, which had been entirely unexplain-

able on the classical theory, was thereby placed in a quite different light, and the predictions of Einstein's theory have received such exact experimental confirmation in recent years, that perhaps the most exact determination of Planck's constant is afforded by measurements on the photoelectric effect. In spite of its heuristic value, however, the hypothesis of light-quanta, which is quite irreconcilable with so-called interference phenomena, is not able to throw light on the nature of radiation. I need only recall that these interference phenomena constitute our only means of investigating the properties of radiation and therefore of assigning any closer meaning to the frequency which in Einstein's theory fixes the magnitude of the light-quantum.

In the following years many efforts were made to apply the concepts of the quantum theory to the question of atomic structure, and the principal emphasis was sometimes placed on one and sometimes on the other of the consequences deduced by Einstein from Planck's result. As the best known of the attempts in this direction, from which, however, no definite results were obtained, I may mention the work of Stark, Sommerfeld, Hasenöhl, Haas, and Nicholson.

From this period also dates an investigation by Bjerrum on infrared absorption bands, which, although it had no direct bearing on atomic structure, proved significant for the development of the quantum theory. He directed attention to the fact that the rotation of the molecules in a gas might be investigated by means of the changes in certain absorption lines with temperature. At the same time he emphasized the fact that the effect should not consist of a continuous widening of the lines such as might be expected from classical theory, which imposed no restrictions on the molecular rotations, but in accordance with the quantum theory he predicted that the lines should be split up into a number of components, corresponding to a sequence of distinct possibilities of rotation. This prediction was confirmed a few years later by Eva von Bahr, and the phenomenon may still be regarded as one of the most striking evidences of the reality of the quantum theory, even though from our present point of view the original explanation has undergone a modification in essential details.

The quantum theory of atomic constitution

The question of further development of the quantum theory was in the meantime placed in a new light by Rutherford's discovery of the atomic nu-

cleus (1911). As we have already seen, this discovery made it quite clear that by classical conceptions alone it was quite impossible to understand the most essential properties of atoms. One was therefore led to seek for a formulation of the principles of the quantum theory that could immediately account for the stability in atomic structure and the properties of the radiation sent out from atoms, of which the observed properties of substances bear witness. Such a formulation was proposed (1913) by the present lecturer in the form of two postulates, which may be stated as follows:

- (1). Among the conceivably possible states of motion in an atomic system there exist a number of so-called stationary states which, in spite of the fact that the motion of the particles in these states obeys the laws of classical mechanics to a considerable extent, possess a peculiar, mechanically unexplainable stability, of such a sort that every permanent change in the motion of the system must consist in a complete transition from one stationary state to another.
- (2). While in contradiction to the classical electromagnetic theory no radiation takes place from the atom in the stationary states themselves, a process of transition between two stationary states can be accompanied by the emission of electromagnetic radiation, which will have the same properties as that which would be sent out according to the classical theory from an electrified particle executing an harmonic vibration with constant frequency. This frequency ν has, however, no simple relation to the motion of the particles of the atom, but is given by the relation

$$h\nu = E' - E'',$$

where h is Planck's constant, and E' and E'' are the values of the energy of the atom in the two stationary states that form the initial and final state of the radiation process. Conversely, irradiation of the atom with electromagnetic waves of this frequency can lead to an absorption process, whereby the atom is transformed back from the latter stationary state to the former.

While the first postulate has in view the general stability of the atom, the second postulate has chiefly in view the existence of spectra with sharp lines. Furthermore, the quantum-theory condition entering in the last postulate affords a starting-point for the interpretation of the laws of series spectra.

The most general of these laws, the combination principle enunciated by Ritz, states that the frequency ν for each of the lines in the spectrum of an element can be represented by the formula

$$\nu = T'' - T',$$

where T'' and T' are two so-called « spectral terms » belonging to a manifold of such terms characteristic of the substance in question.

According to our postulates, this law finds an immediate interpretation in the assumption that the spectrum is emitted by transitions between a number of stationary states in which the numerical value of the energy of the atom is equal to the value of the spectral term multiplied by Planck's constant. This explanation of the combination principle is seen to differ fundamentally from the usual ideas of electrodynamics, as soon as we consider that there is no simple relation between the motion of the atom and the radiation sent out. The departure of our considerations from the ordinary ideas of natural philosophy becomes particularly evident, however, when we observe that the occurrence of two spectral lines, corresponding to combinations of the same spectral term with two other different terms, implies that the nature of the radiation sent out from the atom is not determined only by the motion of the atom at the-beginning.. of the radiation process, but also' depends on the state to which the atom is transferred by the process.

At first glance one might, therefore, think that it would scarcely be possible to bring our formal explanation of the combination principle into direct relation with our views regarding the constitution of the atom, which, indeed, are based on experimental evidence interpreted on classical mechanics and electrodynamics. A closer investigation, however, should make it clear that a definite relation may be obtained between the spectra of the elements and the structure of their atoms on the basis of the postulates.

The hydrogen spectrum

The simplest spectrum we know is that of hydrogen. The frequencies of its lines may be represented with great accuracy by means of Balmer's formula :

$$\nu = K \left(\frac{1}{n''^2} - \frac{1}{n'^2} \right),$$

where K is a constant and n' and n'' are two integers. In the spectrum we accordingly meet a single series of spectral terms of the form K/n^2 , which decrease regularly with increasing term number n . In accordance with the postulates, we shall therefore assume that each of the hydrogen lines is emitted by a transition between two states belonging to a series of stationary states of the hydrogen atom in which the numerical value of the atom's energy is equal to hK/n^2 .

Following our picture of atomic structure, a hydrogen atom consists of a positive nucleus and an electron which - so far as ordinary mechanical conceptions are applicable - will with great approximation describe a periodic elliptical orbit with the nucleus at one focus. The major axis of the orbit is inversely proportional to the work necessary completely to remove the electron from the nucleus, and, in accordance with the above, this work in the stationary states is just equal to hK/n^2 . We thus arrive at a manifold of stationary states for which the major axis of the electron orbit takes on a series of discrete values proportional to the squares of the whole numbers. The accompanying Fig. 2 shows these relations diagrammatically. For the sake of simplicity the electron orbits in the stationary states are represented by circles, although in reality the theory places no restriction on the eccentricity of the orbit, but only determines the length of the major axis. The arrows represent the transition processes that correspond to the red and

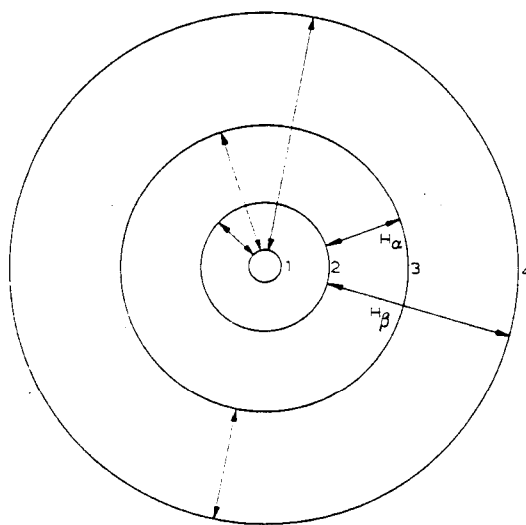


Fig. 2.

green hydrogen lines, H_{α} and H_{β} , the frequency of which is given by means of the Balmer formula when we put $n'' = 2$ and $n' = 3$ and 4 respectively. The transition processes are also represented which correspond to the first three lines of the series of ultraviolet lines found by Lyman in 1914, of which the frequencies are given by the formula when n is put equal to 1 , as well as to the first line of the infrared series discovered some years previously by Paschen, which are given by the formula if n'' is put equal to 3 .

This explanation of the origin of the hydrogen spectrum leads us quite naturally to interpret this spectrum as the manifestation of a process whereby the electron is bound to the nucleus. While the largest spectral term with term number 1 corresponds to the final stage in the binding process, the small spectral terms that have larger values of the term number correspond to stationary states which represent the initial states of the binding process, where the electron orbits still have large dimensions, and where the work required to remove an electron from the nucleus is still small. The final stage in the binding process we may designate as the normal state of the atom, and it is distinguished from the other stationary states by the property that, in accordance with the postulates, the state of the atom can only be changed by the addition of energy whereby the electron is transferred to an orbit of larger dimensions corresponding to an earlier stage of the binding process.

The size of the electron orbit in the normal state calculated on the basis of the above interpretation of the spectrum agrees roughly with the value for the dimensions of the atoms of the elements that have been calculated by the kinetic theory of matter from the properties of gases. Since, however, as an immediate consequence of the stability of the stationary states that is claimed by the postulates, we must suppose that the interaction between two atoms during a collision cannot be completely described with the aid of the laws of classical mechanics, such a comparison as this cannot be carried further on the basis of such considerations as those just outlined.

A more intimate connexion between the spectra and the atomic model has been revealed, however, by an investigation of the motion in those stationary states where the term number is large, and where the dimensions of the electron orbit and the frequency of revolution in it vary relatively little when we go from one stationary state to the next following. It was possible to show that the frequency of the radiation sent out during the transition between two stationary states, the difference of the term numbers of which is small in comparison to these numbers themselves, tended to coincide in frequency with one of the harmonic components into which the

electron motion could be resolved, and accordingly also with the frequency of one of the wave trains in the radiation which would be emitted according to the laws of ordinary electrodynamics.

The condition that such a coincidence should occur in this region where the stationary states differ but little from one another proves to be that the constant in the Balmer formula can be expressed by means of the relation

$$K = \frac{2\pi^2 e^4 m}{h^3},$$

where e and m are respectively the charge and mass of the electron, while h is Planck's constant. This relation has been shown to hold to within the considerable accuracy with which, especially through the beautiful investigations of Millikan, the quantities e , m , and h are known.

This result shows that there exists a connexion between the hydrogen spectrum and the model for the hydrogen atom which, on the whole, is as close as we might hope considering the departure of the postulates from the classical mechanical and electrodynamic laws. At the same time, it affords some indication of how we may perceive in the quantum theory, in spite of the fundamental character of this departure, a natural generalization of the fundamental concepts of the classical electrodynamic theory. To this most important question we shall return later, but first we will discuss how the interpretation of the hydrogen spectrum on the basis of the postulates has proved suitable in several ways, for elucidating the relation between the properties of the different elements.

Relationships between the elements

The discussion above can be applied immediately to the process whereby an electron is bound to a nucleus with any given charge. The calculations show that, in the stationary state corresponding to a given value of the number n , the size of the orbit will be inversely proportional to the nuclear charge, while the work necessary to remove an electron will be directly proportional to the square of the nuclear charge. The spectrum that is emitted during the binding of an electron by a nucleus with charge N times that of the hydrogen nucleus can therefore be represented by the formula:

$$\nu = N^2 K \left(\frac{1}{n'^2} - \frac{1}{n''^2} \right).$$

If in this formula we put $N = 2$, we get a spectrum which contains a set of lines in the visible region which was observed many years ago in the spectrum of certain stars. Rydberg assigned these lines to hydrogen because of the close analogy with the series of lines represented by the Balmer formula. It was never possible to produce these lines in pure hydrogen, but just before the theory for the hydrogen spectrum was put forward, Fowler succeeded in observing the series in question by sending a strong discharge through a mixture of hydrogen and helium. This investigator also assumed that the lines were hydrogen lines, because there existed no experimental evidence from which it might be inferred that two different substances could show properties resembling each other so much as the spectrum in question and that of hydrogen. After the theory was put forward, it became clear, however, that the observed lines must belong to a spectrum of helium, but that they were not like the ordinary helium spectrum emitted from the neutral atom. They came from an ionized helium atom which consists of a single electron moving about a nucleus with double charge. In this way there was brought to light a new feature of the relationship between the elements, which corresponds exactly with our present ideas of atomic structure, according to which the physical and chemical properties of an element depend in the first instance only on the electric charge of the atomic nucleus.

Soon after this question was settled the existence of a similar general relationship between the properties of the elements was brought to light by Moseley's well-known investigations on the characteristic X-ray spectra of the elements, which was made possible by Laue's discovery of the interference of X-rays in crystals and the investigations of W. H. and W. L. Bragg on this subject. It appeared, in fact, that the X-ray spectra of the different elements possessed a much simpler structure and a much greater mutual resemblance than their optical spectra. In particular, it appeared that the spectra changed from element to element in a manner that corresponded closely to the formula given above for the spectrum emitted during the binding of an electron to a nucleus, provided N was put equal to the atomic number of the element concerned. This formula was even capable of expressing, with an approximation that could not be without significance, the frequencies of the strongest X-ray lines, if small whole numbers were substituted for n' and n'' .

This discovery was of great importance in several respects. In the first place, the relationship between the X-ray spectra of different elements proved so simple that it became possible to fix without ambiguity the atomic number for all known substances, and in this way to predict with certainty the atomic number of all such hitherto unknown elements for which there is a place in the natural system. Fig. 3 shows how the square root of the frequency for two characteristic X-ray lines depends on the atomic number. These lines belong to the group of so-called K-lines, which are the most penetrating of the characteristic rays. With very close approximation the points lie on straight lines, and the fact that they do so is conditioned not only by our taking account of known elements, but also by our leaving an open place between molybdenum (42) and ruthenium (44), just as in Mendeleev's original scheme of the natural system of the elements.

Further, the laws of X-ray spectra provide a confirmation of the general theoretical conceptions, both with regard to the constitution of the atom and the ideas that have served as a basis for the interpretation of spectra. Thus

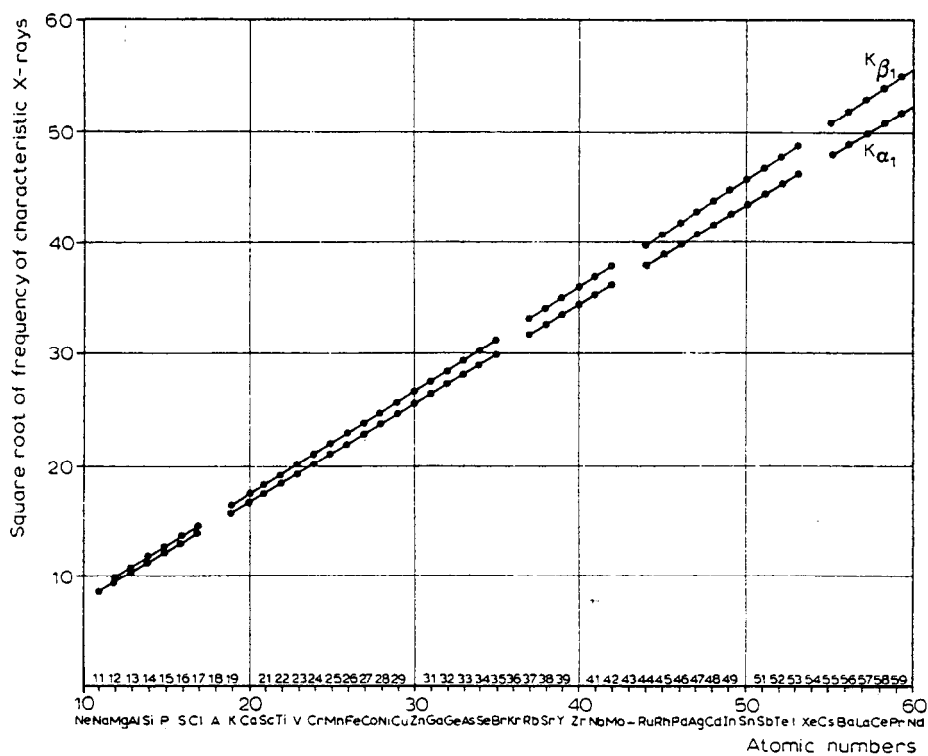


Fig. 3.

the similarity between X-ray spectra and the spectra emitted during the binding of a single electron to a nucleus may be simply interpreted from the fact that the transitions between stationary states with which we are concerned in X-ray spectra are accompanied by changes in the motion of an electron in the inner part of the atom, where the influence of the attraction of the nucleus is very great compared with the repulsive forces of the other electrons.

The relations between other properties of the elements are of a much more complicated character, which originates in the fact that we have to do with processes concerning the motion of the electrons in the outer part of the atom, where the forces that the electrons exert on one another are of the same order of magnitude as the attraction towards the nucleus, and where, therefore, the details of the interaction of the electrons play an important part. A characteristic example of such a case is afforded by the spatial extension of the atoms of the elements. Lothar Meyer himself directed attention to the characteristic periodic change exhibited by the ratio of the atomic weight to the density, the so-called atomic volume, of the elements in the natural system. An idea of these facts is given by Fig. 4, in which the atomic volume is represented as a function of the atomic number. A greater difference be-

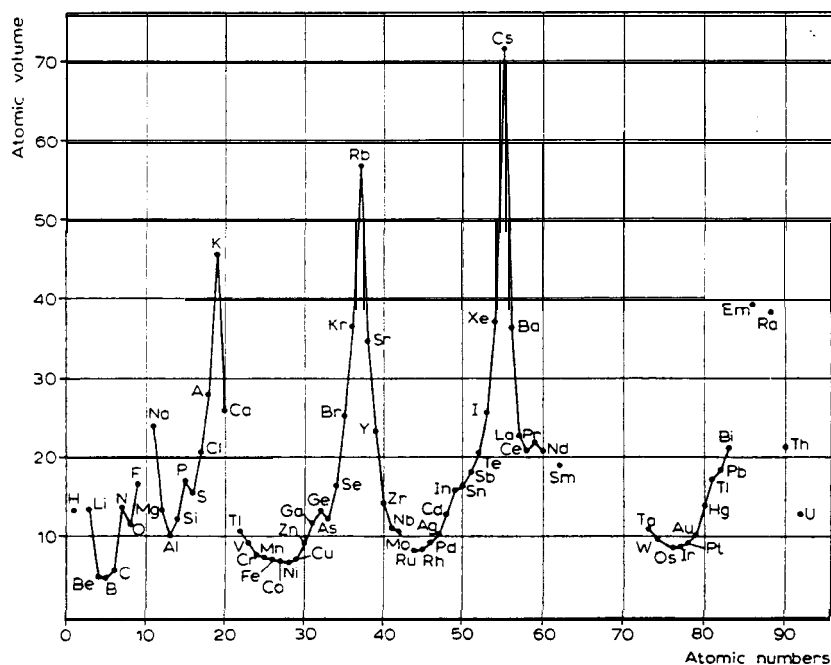


Fig. 4.

tween this and the previous figure could scarcely be imagined. While the X-ray spectra vary uniformly with the atomic number, the atomic volumes show a characteristic periodic change which corresponds exactly to the change in the chemical properties of the elements.

Ordinary optical spectra behave in an analogous way. In spite of the dissimilarity between these spectra, Rydberg succeeded in tracing a certain general relationship between the hydrogen spectrum and other spectra. Even though the spectral lines of the elements with higher atomic number appear as combinations of a more complicated manifold of spectral terms which is not so simply co-ordinated with a series of whole numbers, still the spectral terms can be arranged in series each of which shows a strong similarity to the series of terms in the hydrogen spectrum. This similarity appears in the fact that the terms in each series can, as Rydberg pointed out, be very accurately represented by the formula $K/(n + \alpha)^2$, where K is the same constant that occurs in the hydrogen spectrum, often called the Rydberg constant, while n is the term number, and α a constant which is different for the different series.

This relationship with the hydrogen spectrum leads us immediately to regard these spectra as the *last step of a process whereby the neutral atom is built up by the capture and binding of electrons to the nucleus, one by one*. In fact, it is clear that the last electron captured, so long as it is in that stage of the binding process in which its orbit is still large compared to the orbits of the previously bound electrons, will be subjected to a force from the nucleus and these electrons, that differs but little from the force with which the electron in the hydrogen atom is attracted towards the nucleus while it is moving in an orbit of corresponding dimensions.

The spectra so far considered, for which Rydberg's laws hold, are excited by means of electric discharge under ordinary conditions and are often called arc spectra. The elements emit also another type of spectrum, the so-called spark spectra, when they are subjected to an extremely powerful discharge. Hitherto it was impossible to disentangle the spark spectra in the same way as the arc spectra. Shortly after the above view on the origin of arc spectra was brought forward, however, Fowler found (1914) that an empirical expression for the spark spectrum lines could be established which corresponds exactly to Rydberg's laws with the single difference that the constant K is replaced by a constant four times as large. Since, as we have seen, the constant that appears in the spectrum sent out during the binding of an electron to a helium nucleus is exactly equal to $4K$, it becomes evident that spark

spectra are due to the ionized atom, and that their emission corresponds to *the last step but one in the formation of the neutral atom* by the successive capture and binding of electrons.

Absorption and excitation of spectral lines

The interpretation of the origin of the spectra was also able to explain the characteristic laws that govern absorption spectra. As Kirchhoff and Bunsen had already shown, there is a close relation between the selective absorption of substances for radiation and their emission spectra, and it is on this that the application of spectrum analysis to the heavenly bodies essentially rests. Yet on the basis of the classical electromagnetic theory, it is impossible to understand why substances in the form of vapour show absorption for certain lines in their emission spectrum and not for others.

On the basis of the postulates given above we are, however, led to assume that the absorption of radiation corresponding to a spectral line emitted by a transition from one stationary state of the atom to a state of less energy is brought about by the return of the atom from the last-named state to the first. We thus understand immediately that in ordinary circumstances a gas or vapour can only show selective absorption for spectral lines that are produced by a transition from a state corresponding to an earlier stage in the binding process to the normal state. Only at higher temperatures or under the influence of electric discharges whereby an appreciable number of atoms are being constantly disrupted from the normal state, can we expect absorption for other lines in the emission spectrum in agreement with the experiments.

A most direct confirmation for the general interpretation of spectra on the basis of the postulates has also been obtained by investigations on the excitation of spectral lines and ionization of atoms by means of impact of free electrons with given velocities. A decided advance in this direction was marked by the well-known investigations of Franck and Hertz (1914). It appeared from their results that by means of electron impacts it was impossible to impart to an atom an arbitrary amount of energy, but only such amounts as corresponded to a transfer of the atom from its normal state to another stationary state of the existence of which the spectra assure us, and the energy of which can be inferred from the magnitude of the spectral term.

Further, striking evidence was afforded of the independence that, accord-

ing to the postulates, must be attributed to the processes which give rise to the emission of the different spectral lines of an element. Thus it could be shown directly that atoms that were transferred in this manner to a stationary state of greater energy were able to return to the normal state with emission of radiation corresponding to a single spectral line.

Continued investigations on electron impacts, in which a large number of physicists have shared, have also produced a detailed confirmation of the theory concerning the excitation of series spectra. Especially it has been possible to show that for the *ionization* of an atom by electron impact an amount of energy is necessary that is exactly equal to the work required, according to the theory, to remove the last electron captured from the atom. This work can be determined directly as the product of Planck's constant and the spectral term corresponding to the normal state, which, as mentioned above, is equal to the limiting value of the frequencies of the spectral series connected with selective absorption.

The quantum theory of multiply-periodic systems

While it was thus possible by means of the fundamental postulates of the quantum theory to account directly for certain general features of the properties of the elements, a closer development of the ideas of the quantum theory was necessary in order to account for these properties in further detail. In the course of the last few years a more general theoretical basis has been attained through the development of formal methods that permit the fixation of the stationary states for electron motions of a more general type than those we have hitherto considered. For a simply periodic motion such as we meet in the pure harmonic oscillator, and at least to a first approximation, in the motion of an electron about a positive nucleus, the manifold of stationary states can be simply co-ordinated to a series of whole numbers. For motions of the more general class mentioned above, the so-called *multiply-periodic* motions, however, the stationary states compose a more complex manifold, in which, according to these formal methods, each state is characterized by several whole numbers, the so-called ((quantum numbers)).

In the development of the theory a large number of physicists have taken part, and the introduction of several quantum numbers can be traced back to the work of Planck himself. But the definite step which gave the impetus to further work was made by Sommerfeld (1915) in his explanation of the

fine structure shown by the hydrogen lines when the spectrum is observed with a spectroscope of high resolving power. The occurrence of this fine structure must be ascribed to the circumstance that we have to deal, even in hydrogen, with a motion which is not exactly simply periodic. In fact, as a consequence of the change in the electron's mass with velocity that is claimed by the theory of relativity, the electron orbit will undergo a very slow precession in the orbital plane. The motion will therefore be doubly periodic, and besides a number characterizing the term in the Balmer formula, which we shall call the *principal quantum number* because it determines in the main the energy of the atom, the fixation of the stationary states demands another quantum number which we shall call the *subordinate quantum number*.

A survey of the motion in the stationary states thus fixed is given in the diagram (Fig. 5), which reproduces the relative size and form of the electron orbits. Each orbit is designated by a symbol n_k , where n is the principal quantum number and k the subordinate quantum number. All orbits with the same principal quantum number have, to a first approximation, the same major axis, while orbits with the same value of k have the same parameter, i.e. the same value for the shortest chord through the focus. Since the energy values for different states with the same value of n but different values of k differ a little from each other, we get for each hydrogen line corresponding to definite values of n' and n'' in the Balmer formula a number of different transition processes, for which the frequencies of the emitted radia-

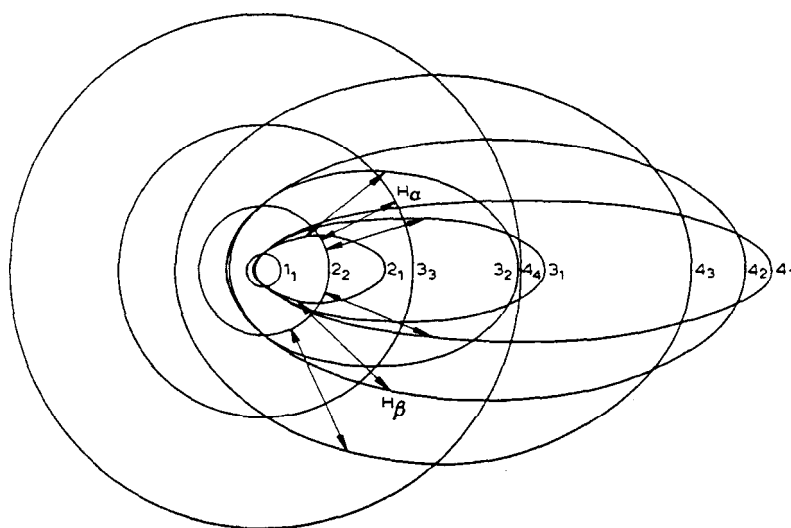


Fig. 5.

tion as calculated by the second postulate are not exactly the same. As Sommerfeld was able to show, the components this gives for each hydrogen line agree with the observations on the fine structure of hydrogen lines to within the limits of experimental error. In the figure the arrows designate the processes that give rise to the components of the red and green lines in the hydrogen spectrum, the frequencies of which are obtained by putting $n'' = 2$ and $n' = 3$ or 4 respectively in the Balmer formula.

In considering the figure it must not be forgotten that the description of the orbit is there incomplete, in so much as with the scale used the slow precession does not show at all. In fact, this precession is so slow that even for the orbits that rotate most rapidly the electron performs about 40,000 revolutions before the perihelion has gone round once. Nevertheless, it is this precession alone that is responsible for the multiplicity of the stationary states characterized by the subordinate quantum number. If, for example, the hydrogen atom is subjected to a small disturbing force which perturbs the regular precession, the electron orbit in the stationary states will have a form altogether different from that given in the figure. This implies that the fine structure will change its character completely, but the hydrogen spectrum will continue to consist of lines that are given to a close approximation by the Balmer formula, due to the fact that the approximately periodic character of the motion will be retained. Only when the disturbing forces become so large that even during a single revolution of the electron the orbit is appreciably disturbed, will the spectrum undergo essential changes. The statement often advanced that the introduction of two quantum numbers should be a necessary condition for the explanation of the Balmer formula must therefore be considered as a misconception of the theory.

Sommerfeld's theory has proved itself able to account not only for the fine structure of the hydrogen lines, but also for that of the lines in the helium spark spectrum. Owing to the greater velocity of the electron, the intervals between the components into which a line is split up are here much greater and can be measured with much greater accuracy. The theory was also able to account for certain features in the fine structure of X-ray spectra, where we meet frequency differences that may even reach a value more than a million times as great as those of the frequency differences for the components of the hydrogen lines.

Shortly after this result had been attained, Schwarzschild and Epstein (1916) simultaneously succeeded, by means of similar considerations, in accounting for the characteristic changes that the hydrogen lines undergo in

an electric field, which had been discovered by Stark in the year 1914. Next, an explanation of the essential features of the Zeeman effect for the hydrogen lines was worked out at the same time by Sommerfeld and Debye (1917). In this instance the application of the postulates involved the consequence that only certain orientations of the atom relative to the magnetic field were allowable, and this characteristic consequence of the quantum theory has quite recently received a most direct confirmation in the beautiful researches of Stern and Gerlach on the deflexion of swiftly moving silver atoms in a nonhomogenous magnetic field.

The correspondence principle

While this development of the theory of spectra was based on the working out of formal methods for the fixation of stationary states, the present lecturer succeeded shortly afterwards in throwing light on the theory from a new viewpoint, by pursuing further the characteristic connexion between the quantum theory and classical electrodynamics already traced out in the hydrogen spectrum. In connexion with the important work of Ehrenfest and Einstein these efforts led to the formulation of the so-called *correspondence principle*, according to which the occurrence of transitions between the stationary states accompanied by emission of radiation is traced back to the harmonic components into which the motion of the atom may be resolved and which, according to the classical theory, determine the properties of the radiation to which the motion of the particles gives rise.

According to the correspondence principle, it is assumed that every transition process between two stationary states can be co-ordinated with a corresponding harmonic vibration component in such a way that the probability of the occurrence of the transition is dependent on the amplitude of the vibration. The state of polarization of the radiation emitted during the transition depends on the further characteristics of the vibration, in a manner analogous to that in which on the classical theory the intensity and state of polarization in the wave system emitted by the atom as a consequence of the presence of this vibration component would be determined respectively by the amplitude and further characteristics of the vibration.

With the aid of the correspondence principle it has been possible to confirm and to extend the above-mentioned results. Thus it was possible to develop a complete quantum theory explanation of the Zeeman effect for the

hydrogen lines, which, in spite of the essentially different character of the assumptions that underlie the two theories, is very similar throughout to Lorentz's original explanation based on the classical theory. In the case of the Stark effect, where, on the other hand, the classical theory was completely at a loss, the quantum theory explanation could be so extended with the help of the correspondence principle as to account for the polarization of the different components into which the lines are split, and also for the characteristic intensity distribution exhibited by the components. This last question has been more closely investigated by Kramers, and the accompanying figure will give some impression of how completely it is possible to account for the phenomenon under consideration.

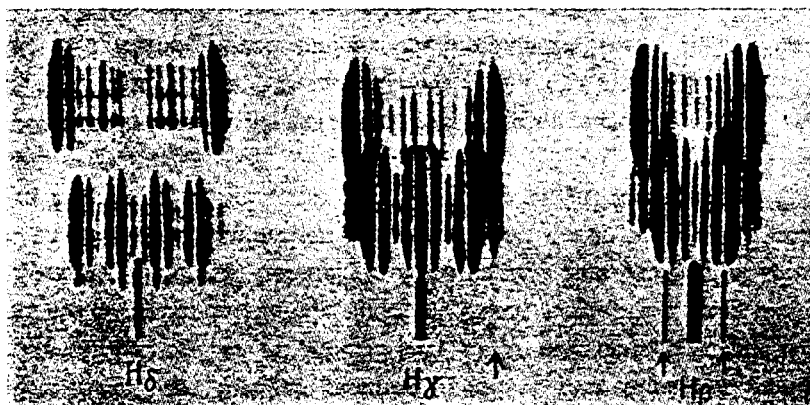


Fig. 6.

Fig. 6 reproduces one of Stark's well-known photographs of the splitting up of the hydrogen lines. The picture displays very well the varied nature of the phenomenon, and shows in how peculiar a fashion the intensity varies from component to component. The components below are polarized perpendicular to the field, while those above are polarized parallel to the field.

Fig. 7 gives a diagrammatic representation of the experimental and theoretical results for the line $H\gamma$, the frequency of which is given by the Balmer formula with $n'' = 2$ and $n' = 5$. The vertical lines denote the components into which the line is split up, of which the picture on the right gives the components which are polarized parallel to the field and that on the left those that are polarized perpendicular to it. The experimental results are represented in the upper half of the diagram, the distances from the dotted line representing the measured displacements of the components, and the lengths

of the lines being proportional to the relative intensity as estimated by Stark from the blackening of the photographic plate. In the lower half is given for comparison a representation of the theoretical results from a drawing in Kramers' paper.

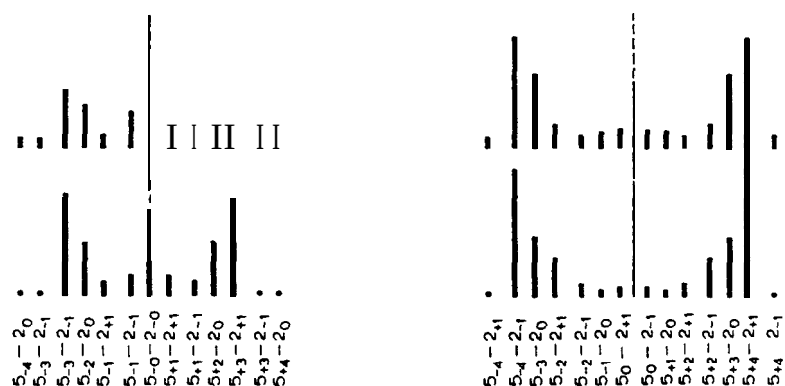


Fig. 7.

The symbol $(n'_s - n''_s)$ attached to the lines gives the transitions between the stationary states of the atom in the electric field by which the components are emitted. Besides the principal quantum integer n , the stationary states are further characterized by a subordinate quantum integer s , which can be negative as well as positive and has a meaning quite different from that of the quantum number k occurring in the relativity theory of the fine structure of the hydrogen lines, which fixed the form of the electron orbit in the undisturbed atom. Under the influence of the electric field both the form of the orbit and its position undergo large changes, but certain properties of the orbit remain unchanged, and the subordinate quantum number s is connected with these. In Fig. 7 the position of the components corresponds to the frequencies calculated for the different transitions, and the lengths of the lines are proportional to the probabilities as calculated on the basis of the correspondence principle, by which also the polarization of the radiation is determined. It is seen that the theory reproduces completely the main feature of the experimental results, and in the light of the correspondence principle we can say that the Stark effect reflects down to the smallest details the action of the electric field on the orbit of the electron in the hydrogen atom, even though in this case the reflection is so distorted that, in contrast with the case of the Zeeman effect, it would scarcely be possible directly to

recognize the motion on the basis of the classical ideas of the origin of electromagnetic radiation.

Results of interest were also obtained for the spectra of elements of higher atomic number, the explanation of which in the meantime had made important progress through the work of Sommerfeld, who introduced several quantum numbers for the description of the electron orbits. Indeed, it was possible, with the aid of the correspondence principle, to account completely for the characteristic rules which govern the seemingly capricious occurrence of combination lines, and it is not too much to say that the quantum theory has not only provided a simple interpretation of the combination principle, but has further contributed materially to the clearing up of the mystery that has long rested over the application of this principle.

The same viewpoints have also proved fruitful in the investigation of the so-called band spectra. These do not originate, as do series spectra, from individual atoms, but from molecules; and the fact that these spectra are so rich in lines is due to the complexity of the motion entailed by the vibrations of the atomic nuclei relative to each other and the rotations of the molecule as a whole. The first to apply the postulates to this problem was Schwarzschild, but the important work of Heurhnger especially has thrown much light on the origin and structure of band spectra. The considerations employed here can be traced back directly to those discussed at the beginning of this lecture in connexion with Bjerrum's theory of the influence of molecular rotation on the infrared absorption lines of gases. It is true we no longer think that the rotation is reflected in the spectra in the way claimed by classical electrodynamics, but rather that the line components are due to transitions between stationary states which differ as regards rotational motion. That the phenomenon retains its essential feature, however, is a typical consequence of the correspondence principle.

The natural system of the elements

The ideas of the origin of spectra outlined in the preceding have furnished the basis for a theory of the structure of the atoms of the elements which has shown itself suitable for a general interpretation of the main features of the properties of the elements, as exhibited in the natural system. This theory is based primarily on considerations of the manner in which the atom can be imagined to be built up by the capture and binding of electrons to the nu-

cleus, one by one. As we have seen, the optical spectra of elements provide us with evidence on the progress of the last steps in this building-up process.

An insight into the kind of information that the closer investigation of the spectra has provided in this respect may be obtained from Fig. 8, which gives a diagrammatic representation of the orbital motion in the stationary states corresponding to the emission of the arc-spectrum of potassium. The curves show the form of the orbits described in the stationary states by the last electron captured in the potassium atom, and they can be considered as stages in the process whereby the 19th electron is bound after the 18 previous electrons have already been bound in their normal orbits. In order not to complicate the figure, no attempt has been made to draw any of the orbits of these inner electrons, but the region in which they move is enclosed by a dotted circle. In an atom with several electrons the orbits will, in general, have a complicated character. Because of the symmetrical nature of the field of force about the nucleus, however, the motion of each single electron can be approximately described as a plane periodic motion on which is superimposed a uniform rotation in the plane of the orbit. The orbit of each electron will therefore be to a first approximation doubly periodic, and will be fixed by two quantum numbers, as are the stationary states in a hydrogen atom when the relativity precession is taken into account.

In Fig. 8, as in Fig. 5, the electron orbits are marked with the symbol n_k ,

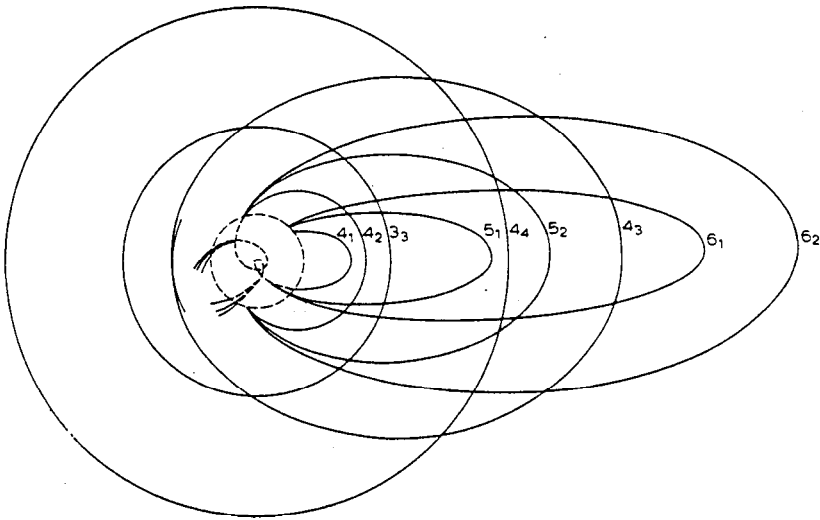


Fig. 8.

where n is the principal quantum number and k the subordinate quantum number. While for the initial states of the binding process, where the quantum numbers are large, the orbit of the last electron captured lies completely outside of those of the previously bound electrons, this is not the case for the last stages. Thus, in the potassium atom, the electron orbits with subordinate quantum numbers 2 and 1 will, as indicated in the figure, penetrate partly into the inner region. Because of this circumstance, the orbits will deviate very greatly from a simple Kepler motion, since they will consist of a series of successive outer loops that have the same size and form, but each of which is turned through an appreciable angle relative to the preceding one. Of these outer loops only one is shown in the figure. Each of them coincides very nearly with a piece of a Kepler ellipse, and they are connected, as indicated, by a series of inner loops of a complicated character in which the electron approaches the nucleus closely. This holds especially for the orbit with subordinate quantum number 1, which, as a closer investigation shows, will approach nearer to the nucleus than any of the previously bound electrons.

On account of this penetration into the inner region, the strength with which an electron in such an orbit is bound to the atom will - in spite of the fact that for the most part it moves in a field of force of the same character as that surrounding the hydrogen nucleus - be much greater than for an electron in a hydrogen atom that moves in an orbit with the same principal quantum number, the maximum distance of the electron from the nucleus at the same time being considerably less than in such a hydrogen orbit. As we shall see, this feature of the binding process in atoms with many electrons is of essential importance in order to understand the characteristic periodic way in which many properties of the elements as displayed in the natural system vary with the atomic number.

In the accompanying table (Fig. 9) given a summary of the results concerning the structure of the atoms of the elements to which the author has been led by a consideration of successive capture and binding of electrons to the atomic nucleus. The figures before the different elements are the atomic numbers, which give the total number of electrons in the neutral atom. The figures in the different columns give the number of electrons in orbits corresponding to the values of the principal and subordinate quantum numbers standing at the top. In accordance with ordinary usage we will, for the sake of brevity, designate an orbit with principal quantum number n as an n -quantum orbit. The first electron bound in each atom moves in an orbit

	1 ₁	2 ₁ 2 ₂	3 ₁ 3 ₂ 3 ₃	4 ₁ 4 ₂ 4 ₃ 4 ₄	5 ₁ 5 ₂ 5 ₃ 5 ₄ 5 ₅	6 ₁ 6 ₂ 6 ₃ 6 ₄ 6 ₅ 6 ₆	7 ₁ 7 ₂
1 H	1						
2 He	2						
3 Li	2	1					
4 Be	2	2					
5 B	2	2 (1)					
- -	-	-					
10 Ne	2	4 4					
11 Na	2	4 4	1				
12 Mg	2	4 4	2				
13 Al	2	4 4	2 1				
- -	-	-	-				
18 A	2	4 4	4 4				
19 K	2	4 4	4 4	1			
20 Ca	2	4 4	4 4	2			
21 Sc	2	4 4	4 4 1	(2)			
22 Ti	2	4 4	4 4 2	(2)			
- -	-	-	-	-			
29 Cu	2	4 4	6 6 6	1			
30 Zn	2	4 4	6 6 6	2			
31 Ga	2	4 4	6 6 6	2 1			
- -	-	-	-	-			
36 Kr	2	4 4	6 6 6	4 4			
37 Rb	2	4 4	6 6 6	4 4	1		
38 Sr	2	4 4	6 6 6	4 4	2		
39 Y	2	4 4	6 6 6	4 4 1	(2)		
40 Zr	2	4 4	6 6 6	4 4 2	(2)		
- -	-	-	-	-	-		
47 Ag	2	4 4	6 6 6	6 6 6	1		
48 Cd	2	4 4	6 6 6	6 6 6	2		
49 In	2	4 4	6 6 6	6 6 6	2 1		
- -	-	-	-	-	-		
54 X	2	4 4	6 6 6	6 6 6	4 4		
55 Cs	2	4 4	6 6 6	6 6 6	4 4	1	
56 Ba	2	4 4	6 6 6	6 6 6	4 4	2	
57 La	2	4 4	6 6 6	6 6 6	4 4 1	(2)	
58 Ce	2	4 4	6 6 6	6 6 6 1	4 4 1	(2)	
59 Pr	2	4 4	6 6 6	6 6 6 2	4 4 1	(2)	
- -	-	-	-	-	-	-	
71 Cp	2	4 4	6 6 6	8 8 8 8	4 4 1	(2)	
72 -	2	4 4	6 6 6	8 8 8 8	4 4 2	(2)	
- -	-	-	-	-	-	-	
79 Au	2	4 4	6 6 6	8 8 8 8	6 6 6		
80 Hg	2	4 4	6 6 6	8 8 8 8	6 6 6	2	
81 Tl	2	4 4	6 6 6	8 8 8 8	6 6 6	2 1	
- -	-	-	-	-	-	-	
86 Em	2	4 4	6 6 6	8 8 8 8	6 6 6	4 4	
87 -	2	4 4	6 6 6	8 8 8 8	6 6 6	4 4	1
88 Ra	2	4 4	6 6 6	8 8 8 8	6 6 6	4 4	2
89 Ac	2	4 4	6 6 6	8 8 8 8	6 6 6	4 4 1	(2)
90 Th	2	4 4	6 6 6	8 8 8 8	6 6 6	4 4 2	(2)
- -	-	-	-	-	-	-	-
118 ?	2	4 4	6 6 6	8 8 8 8	8 8 8 8	6 6 6	4 4

Fig. 9.

that corresponds to the normal state of the hydrogen atom with quantum symbol $1s$. In the hydrogen atom there is of course only one electron; but we must assume that in the atoms of other elements the next electron also will be bound in such a s -quantum orbit of type $1s$. As the table shows, the following electrons are bound in p -quantum orbits. To begin with, the binding will result in a $2p$ orbit, but later electrons will be bound in $3p$ orbits, until, after binding the first 10 electrons in the atom, we reach a closed configuration of the d -quantum orbits in which we assume there are four orbits of each type. This configuration is met for the first time in the neutral neon atom, which forms the conclusion of the second period in the system of the elements. When we proceed in this system, the following electrons are bound in f -quantum orbits, until, after the conclusion of the third period of the system, we encounter for the first time, in elements of the fourth period, electrons in g -quantum orbits, and so on.

This picture of atomic structure contains many features that were brought forward by the work of earlier investigators. Thus the attempt to interpret the relations between the elements in the natural system by the assumption of a division of the electrons into groups goes as far back as the work of J. J. Thomson in 1904. Later, this viewpoint was developed chiefly by Kossel (1916), who, moreover, has connected such a grouping with the laws that investigations of X-ray spectra have brought to light.

Also G. R. Lewis and I. Langmuir have sought to account for the relations between the properties of the elements on the basis of a grouping inside the atom. These investigators, however, assumed that the electrons do not move about the nucleus, but occupy positions of equilibrium. In this way, though, no closer relation can be reached between the properties of the elements and the experimental results concerning the constituents of the atoms. Statical positions of equilibrium for the electrons are in fact not possible in cases in which the forces between the electrons and the nucleus even approximately obey the laws that hold for the attractions and repulsions between electrical charges.

The possibility of an interpretation of the properties of the elements on the basis of these latter laws is quite characteristic for the picture of atomic structure developed by means of the quantum theory. As regards this picture, the idea of connecting the grouping with a classification of electron orbits according to increasing quantum numbers was suggested by Moseley's discovery of the laws of X-ray spectra, and by Sommerfeld's work on the fine structure of these spectra. This has been principally emphasized by Vegard,

who some years ago in connexion with investigations of X-ray spectra proposed a grouping of electrons in the atoms of the elements, which in many ways shows a likeness to that which is given in the above table.

A satisfactory basis for the further development of this picture of atomic structure has, however, only recently been created by the study of the binding processes of the electrons in the atom, of which we have experimental evidence in optical spectra, and the characteristic features of which have been elucidated principally by the correspondence principle. It is here an essential circumstance that the restriction on the course of the binding process, which is expressed by the presence of electron orbits with higher quantum numbers in the normal state of the atom, can be naturally connected with the general condition for the occurrence of transitions between stationary states, formulated in that principle.

Another essential feature of the theory is the influence, on the strength of binding and the dimensions of the orbits, of the penetration of the later bound electrons into the region of the earlier bound ones, of which we have seen an example in the discussion of the origin of the potassium spectrum. Indeed, this circumstance may be regarded as the essential cause of the pronounced periodicity in the properties of the elements, in that it implies that the atomic dimensions and chemical properties of homologous substances in the different periods, as, for example, the alkali-metals, show a much greater similarity than that which might be expected from a direct comparison of the orbit of the last electron bound with an orbit of the same quantum number in the hydrogen atom.

The increase of the principal quantum number which we meet when we proceed in the series of the elements, affords also an immediate explanation of the characteristic deviations from simple periodicity which are exhibited by the natural system and are expressed in Fig. 1 by the bracketing of certain series of elements in the later periods. The first time such a deviation is met with is in the 4th period, and the reason for it can be simply illustrated by means of our figure of the orbits of the last electron bound in the atom of potassium, which is the first element in this period. Indeed, in potassium we encounter for the first time in the sequence of the elements a case in which the principal quantum number of the orbit of the last electron bound is, in the normal state of the atom, larger than in one of the earlier stages of the binding process. The normal state corresponds here to a $4l$ orbit, which, because of the penetration into the inner region, corresponds to a much stronger binding of the electron than a 4-quantum orbit in the hydrogen

atom. The binding in question is indeed even stronger than for a z-quantum orbit in the hydrogen atom, and is therefore more than twice as strong as in the circular 3_z orbit which is situated completely outside the inner region, and for which the strength of the binding differs but little from that for a j-quantum orbit in hydrogen.

This will not continue to be true, however, when we consider the binding of the 19th electron in substances of higher atomic number, because of the much smaller relative difference between the field of force outside and inside the region of the first eighteen electrons bound. As is shown by the investigation of the spark spectrum of calcium, the binding of the 19th electron in the 4_z orbit is here but little stronger than in 3_z orbits, and as soon as we reach scandium, we must assume that the 3_z orbit will represent the orbit of the 19th electron in the normal state, since this type of orbit will correspond to a stronger binding than a 4_z orbit. While the group of electrons in 2-quantum orbits has been entirely completed at the end of the 2nd period, the development that the group of 3-quantum orbits undergoes in the course of the 3rd period can therefore only be described as a provisional completion, and, as shown in the table, this electron group will, in the bracketed elements of the 4th period, undergo a stage of further development in which electrons are added to it in j-quantum orbits.

This development brings in new features, in that the development of the electron group with 4-quantum orbits comes to a standstill, so to speak, until the 3-quantum group has reached its final closed form. Although we are not yet in a position to account in all details for the steps in the gradual development of the 3-quantum electron group, still we can say that with the help of the quantum theory we see at once why it is in the 4th period of the system of the elements that there occur for the first time successive elements with properties that resemble each other as much as the properties of the iron *group*; indeed, we can even understand why these elements show their well-known paramagnetic properties. Without further reference to the quantum theory, Eadenburg had on a previous occasion already suggested the idea of relating the chemical and magnetic properties of these elements with the development of an inner electron group in the atom.

I will not enter into many more details, but only mention that the peculiarities we meet with in the 5th period are explained in much the same way as those in the 4th period. Thus the properties of the bracketed elements in the 5th period as it appears in the table, depend on a stage in the development of the b-quantum electron group that is initiated by the entrance in the

normal state of electrons in 4_3 orbits. In the 6th period, however, we meet new features. In this period we encounter not only a stage of the development of the electron groups with 5- and 6-quantum orbits, but also the final completion of the development of the b-quantum electron group, which is initiated by the entrance for the first time of electron orbits of the 4_4 type in the normal state of the atom. This development finds its characteristic expression in the occurrence of the peculiar family of elements in the 6th period, known as the *rare-earths*. These show, as we know, a still greater mutual similarity in their chemical properties than the elements of the iron family. This must be ascribed to the fact that we have here to do with the development of an electron group that lies deeper in the atom. It is of interest to note that the theory can also naturally account for the fact that these elements, which resemble each other in so many ways, still show great differences in their magnetic properties.

The idea that the occurrence of the rare-earths depends on the development of an inner electron group has been put forward from different sides. Thus it is found in the work of Vegard, and at the same time as my own work, it was proposed by Bury in connexion with considerations of the systematic relation between the chemical properties and the grouping of the electrons inside the atom from the point of view of Langmuir's static atomic model. While until now it has not been possible, however, to give any theoretical basis for such a development of an inner group, we see that our extension of the quantum theory provides us with an unforced explanation. Indeed, it is scarcely an exaggeration to say that if the existence of the rare-earths had not been established by direct chemical investigation, the occurrence of a family of elements of this character within the 6th period of the natural system of the elements might have been theoretically predicted.

When we proceed to the 7th period of the system, we meet for the first time with 7-quantum orbits, and we shall expect to find within this period features that are essentially similar to those in the 6th period, in that besides the first stage in the development of the T-quantum orbits, we must expect to encounter further stages in the development of the group with 6- or 5-quantum orbits. However, it has not been possible directly to confirm this expectation, because only a few elements are known in the beginning of the 7th period. The latter circumstance may be supposed to be intimately connected with the instability of atomic nuclei with large charges, which is expressed in the prevalent radioactivity among elements with high atomic number.

X-ray spectra and atomic constitution

In the discussion of the conceptions of atomic structure we have hitherto placed the emphasis on the formation of the atom by successive capture of electrons. Our picture would, however, be incomplete without some reference to the confirmation of the theory afforded by the study of X-ray spectra. Since the interruption of Moseley's fundamental researches by his untimely death, the study of these spectra has been continued in a most admirable way by Prof. Siegbahn in Lund. On the basis of the large amount of experimental evidence adduced by him and his collaborators, it has been possible recently to give a classification of X-ray spectra that allows an immediate interpretation on the quantum theory. In the first place it has been possible, just as in the case of the optical spectra, to represent the frequency of each of the X-ray lines as the difference between two out of a manifold of spectral terms characteristic of the element in question. Next, a direct connexion with the atomic theory is obtained by the assumption that each of these spectral terms multiplied by Planck's constant is equal to the work which must be done on the atom to remove one of its inner electrons. In fact, the removal of one of the inner electrons from the completed atom may, in accordance with the above considerations on the formation of atoms by capture of electrons, give rise to transition processes by which the place of the electron removed is taken by an electron belonging to one of the more loosely bound electron groups of the atom, with the result that after the transition an electron will be lacking in this latter group.

The X-ray lines may thus be considered as giving evidence of stages in a process by which the atom undergoes a *reorganization* after a disturbance in its interior. According to our views on the stability of the electronic configuration such a disturbance must consist in the removal of electrons from the atom, or at any rate in their transference from normal orbits to orbits of higher quantum numbers than those belonging to completed groups; a circumstance which is clearly illustrated in the characteristic difference between selective absorption in the X-ray region, and that exhibited in the optical region.

The classification of the X-ray spectra, to the achievement of which the above-mentioned work of Sommerfeld and Kossel has contributed materially, has recently made it possible, by means of a closer examination of the manner in which the terms occurring in the X-ray spectra vary with the atomic number, to obtain a very direct test of a number of the theoretical

conclusions as regards the structure of the atom. In Fig. 9 the abscissæ are the atomic numbers and the ordinates are proportional to the square roots of the spectral terms, while the symbols K, L, M, N, O, for the individual

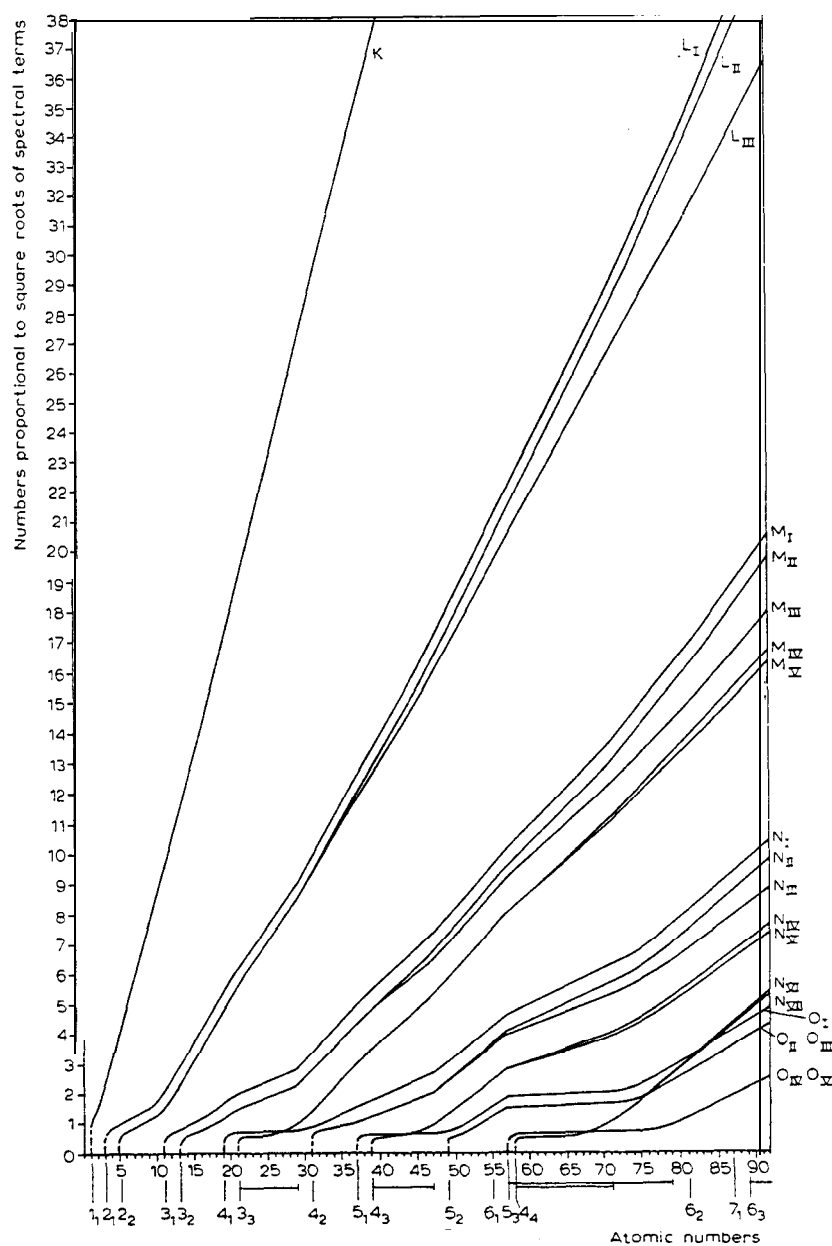


Fig. 10.

terms refer to the characteristic discontinuities in the selective absorption of the elements for X-rays; these were originally found by Barkla before the discovery of the interference of X-rays in crystals had provided a means for the closer investigation of X-ray spectra. Although the curves generally run very uniformly, they exhibit a number of deviations from uniformity which have been especially brought to light by the recent investigation of Coster, who has for some years worked in Siegbahn's laboratory.

These deviations, the existence of which was not discovered until after the publication of the theory of atomic structure discussed above, correspond exactly to what one might expect from this theory. At the foot of the figure the vertical lines indicate where, according to the theory, we should first expect, in the normal state of the atom, the occurrence of n_k orbits of the type designated. We see how it has been possible to connect the occurrence of every spectral term with the presence of an electron moving in an orbit of a definite type, to the removal of which this term is supposed to correspond. That in general there corresponds more than one curve to each type of orbit n_k is due to a complication in the spectra which would lead us too far afield to enter into here, and may be attributed to the deviation from the previously described simple type of motion of the electron arising from the interaction of the different electrons within the same group.

The intervals in the system of the elements, in which a further development of an inner electron group takes place because of the entrance into the normal atom of electron orbits of a certain type, are designated in the figure by the horizontal lines, which are drawn between the vertical lines to which the quantum symbols are affixed. It is clear that such a development of an inner group is everywhere reflected in the curves. Particularly the course of the N- and O-curves may be regarded as a direct indication of that stage in the development of the electron groups with 4-quantum orbits of which the occurrence of the rare-earths bears witness. Although the apparent complete absence of a reflection in the X-ray spectra of the complicated relationships exhibited by most other properties of the elements was the typical and important feature of Moseley's discovery, we can recognize, nevertheless, in the light of the progress of the last years, an intimate connexion between the X-ray spectra and the general relationships between the elements within the natural system.

Before concluding this lecture I should like to mention one further point in which X-ray investigations have been of importance for the test of the theory. This concerns the properties of the hitherto unknown element with

atomic number **72**. On this question opinion has been divided in respect to the conclusions that could be drawn from the relationships within the Periodic Table, and in many representations of the table a place is left open for this element in the rare-earth family. In Julius Thomsen's representation of the natural system, however, this hypothetical element was given a position homologous to titanium and zirconium in much the same way as in our representation in Fig. 1. Such a relationship must be considered as a necessary consequence of the theory of atomic structure developed above, and is expressed in the table (Fig. g) by the fact that the electron configurations for titanium and zirconium show the same sort of resemblances and differences as the electron configurations for zirconium and the element with atomic number **72**. A corresponding view was proposed by Bury on the basis of his above-mentioned systematic considerations of the connexion between the grouping of the electrons in the atom and the properties of the elements.

Recently, however, a communication was published by Dauvillier announcing the observation of some weak lines in the X-ray spectrum of a preparation containing rare-earths. These were ascribed to an element with atomic number **72** assumed to be identical with an element of the rare-earth family, the existence of which in the preparation used had been presumed by Urbain many years ago. This conclusion would, however, if it could be maintained, place extraordinarily great, if not unsurmountable, difficulties in the way of the theory, since it would claim a change in the strength of the binding of the electrons with the atomic number which seems incompatible with the conditions of the quantum theory. In these circumstances Dr. Coster and Prof. Hevesy, who are both for the time working in Copenhagen, took up a short time ago the problem of testing a preparation of zircon-bearing minerals by X-ray spectroscopic analysis. These investigators have been able to establish the existence in the minerals investigated of appreciable quantities of an element with atomic number **72**, the chemical properties of which show a great similarity to those of zirconium and a decided difference from those of the rare-earths.*

I hope that I have succeeded in giving a summary of some of the most important results that have been attained in recent years in the field of atomic theory, and I should like, in concluding, to add a few general remarks concerning the viewpoint from which these results may be judged, and par-

* For the result of the continued work of Coster and Hevesy with the new element, for which they have proposed the name hafnium, the reader may be referred to their letters in Nature of January 20, February 10 and 24, and April 7.

ticularly concerning the question of how far, with these results, it is possible to speak of an explanation, in the ordinary sense of the word. By a theoretical explanation of natural phenomena we understand in general a classification of the observations of a certain domain with the help of analogies pertaining to other domains of observation, where one presumably has to do with simpler phenomena. The most that one can demand of a theory is that this classification can be pushed so far that it can contribute to the development of the field of observation by the prediction of new phenomena.

When we consider the atomic theory, we are, however, in the peculiar position that there can be no question of an explanation in this last sense, since here we have to do with phenomena which from the very nature of the case are simpler than in any other field of observation, where the phenomena are always conditioned by the combined action of a large number of atoms. We are therefore obliged to be modest in our demands and content ourselves with concepts which are formal in the sense that they do not provide a visual picture of the sort one is accustomed to require of the explanations with which natural philosophy deals. Bearing this in mind I have sought to convey the impression that the results, on the other hand, fulfill, at least in some degree, the expectations that are entertained of any theory; in fact, I have attempted to show how the development of atomic theory has contributed to the classification of extensive fields of observation, and by its predictions has pointed out the way to the completion of this classification. It is scarcely necessary, however, to emphasize that the theory is yet in a very preliminary stage, and many fundamental questions still await solution.

Biography

Niels Henrik David Bohr was born in Copenhagen on October 7, 1885, as the son of Christian Bohr, Professor of Physiology at Copenhagen University, and his wife Ellen, née Adler. Niels, together with his younger brother Harald (the future Professor in Mathematics), grew up in an atmosphere most favourable to the development of his genius - his father *was* an eminent physiologist and was largely responsible for awakening his interest in physics while still at school, his mother came from a family distinguished in the field of education.

After matriculation at the Gammelholm Grammar School in 1903, he entered Copenhagen University where he came under the guidance of Professor C. Christiansen, a profoundly original and highly endowed physicist, and took his Master's degree in Physics in 1909 and his Doctor's degree in 1911.

While still a student, the announcement by the Academy of Sciences in Copenhagen of a prize to be awarded for the solution of a certain scientific problem, caused him to take up an experimental and theoretical investigation of the surface tension by means of oscillating fluid jets. This work, which he carried out in his father's laboratory and for which he received the prize offered (a gold medal), was published in the *Transactions of the Royal Society*, **1908**.

Bohr's subsequent studies, however, became more and more theoretical in character, his doctor's disputation being a purely theoretical piece of work on the explanation of the properties of the metals with the aid of the electron theory, which remains to this day a classic on the subject. It was in this work that Bohr was first confronted with the implications of Planck's quantum theory of radiation.

In the autumn of 1911 he made a stay at Cambridge, where he profited by following the experimental work going on in the Cavendish Laboratory under Sir J. J. Thomson's guidance, at the same time as he pursued own theoretical studies. In the spring of 1912 he was at work in Professor Rutherford's laboratory in Manchester, where just in those years such an intensive scientific life and activity prevailed as a consequence of that investigator's funda-

mental inquiries into the radioactive phenomena. Having there carried out a theoretical piece of work on the absorption of alpha rays which was published in the *Philosophical Magazine*, 1913, he passed on to a study of the structure of atoms on the basis of Rutherford's discovery of the atomic nucleus. By introducing conceptions borrowed from the Quantum Theory as established by Planck, which had gradually come to occupy a prominent position in the science of theoretical physics, he succeeded in working out and presenting a picture of atomic structure that, with later improvements (mainly as a result of Heisenberg's ideas in 1925), still fitly serves as an elucidation of the physical and chemical properties of the elements.

In 1913-1914 Bohr held a Lectureship in Physics at Copenhagen University and in 1914-1916 a similar appointment at the Victoria University in Manchester. In 1916 he was appointed Professor of Theoretical Physics at Copenhagen University, and since 1920 (until his death in 1962) he was at the head of the Institute for Theoretical Physics, established for him at that university.

Recognition of his work on the structure of atoms came with the award of the Nobel Prize for 1922.

Bohr's activities in his Institute were since 1930 more and more directed to research on the constitution of the atomic nuclei, and of their transmutations and disintegrations. In 1936 he pointed out that in nuclear processes the smallness of the region in which interactions take place, as well as the strength of these interactions, justify the transition processes to be described more in a classical way than in the case of atoms (Cf. « Neutron capture and nuclear constitution », *Nature*, 137 (1936) 344).

A liquid drop would, according to this view, give a very good picture of the nucleus. This so-called *liquid droplet theory* permitted the understanding of the mechanism of nuclear fission, when the splitting of uranium was discovered by Hahn and Strassmann, in 1939, and formed the basis of important theoretical studies in this field (among others, by Frisch and Meier).

Bohr also contributed to the clarification of the problems encountered in quantum physics, in particular by developing the *concept of complementarity*. Hereby he could show how deeply the changes in the field of physics have affected fundamental features of our scientific outlook and how the consequences of this change of attitude reach far beyond the scope of atomic physics and touch upon all domains of human knowledge. These views are discussed in a number of essays, written during the years 1933-1962. They are available in English, collected in two volumes with the title *Atomic Phys-*

its and Human Knowledge and Essays 1958-1962 on Atomic Physics and Human Knowledge, edited by John Wiley and Sons, New York and London, in 1958 and 1963, respectively.

Among Professor Bohr's numerous writings (some 115 publications), three appearing as books in the English language may be mentioned here as embodying his principal thoughts: *The Theory of Spectra and Atomic Constitution*, University Press, Cambridge, 1922/2nd. ed., 1924; *Atomic Theory and the Description of Nature*, University Press, Cambridge, 1934/reprint 1961; *The Unity of Knowledge*, Doubleday & Co., New York, 1955.

During the Nazi occupation of Denmark in World War II, Bohr escaped to Sweden and spent the last two years of the war in England and America, where he became associated with the Atomic Energy Project. In his later years, he devoted his work to the peaceful application of atomic physics and to political problems arising from the development of atomic weapons. In particular, he advocated a development towards full openness between nations. His views are especially set forth in *his Open Letter to the United Nations*, June 9, 1950.

Until the end, Bohr's mind remained alert as ever; during the last few years of his life he had shown keen interest in the new developments of molecular biology. The latest formulation of his thoughts on the problem of Life appeared in his final (unfinished) article, published after his death: ((Licht und Leben - noch einmal)), *Naturwiss.*, 50 (1963) 725 (in English: « Light and Life revisited », *ICSU Rev.*, 5 (1963) 194).

Niels Bohr was President of the Royal Danish Academy of Sciences, of the Danish Cancer Committee, and Chairman of the Danish Atomic Energy Commission. He was a Foreign Member of the Royal Society (London), the Royal Institution, and Academies in Amsterdam, Berlin, Bologna, Boston, Göttingen, Helsingfors, Budapest, München, Oslo, Paris, Rome, Stockholm, Upsala, Vienna, Washington, Harlem, Moscow, Trondhjem, Halle, Dublin, Liege, and Cracow. He was Doctor, *honoris causa*, of the following universities, colleges, and institutes : (1923-1939) - Cambridge, Liverpool, Manchester, Oxford, Copenhagen, Edinburgh, Kiel, Providence, California, Oslo, Birmingham, London; (1945-1962) - Sorbonne (Paris), Princeton, McGill (Montreal), Glasgow, Aberdeen, Athens, Lund, New York, Basel, Aarhus, Macalester (St. Paul), Minnesota, Roosevelt (Chicago, Ill.), Zagreb, Technion (Haifa), Bombay, Calcutta, Warsaw, Brussels, Harvard, Cambridge (Mass.), and Rockefeller (New York).

Professor Bohr was married, in 1912, to Margrethe Nørlund, who was

for him an ideal companion. They had six sons, of whom they lost two ; the other four have made distinguished careers in various professions-Hans Henrik (M.D.), Erik (chemical engineer), Aage (Ph.D., theoretical physicist, following his father as Director of the Institute for Theoretical Physics), Ernest (lawyer).

Niels Bohr died in Copenhagen on November 18, **1962**.

Physics 1923

ROBERT ANDREWS MILLIKAN

*«for his work on the elementary charge of electricity and on the
photoelectric effect»*

Physics 1923

Presentation Speech by Professor A. Gullstrand, Chairman of the Nobel Committee for Physics of the Royal Swedish Academy of Sciences

Your Majesty, Your Royal Highnesses, Ladies and Gentlemen.

The Royal Academy of Sciences has awarded this year's Nobel Prize for Physics to Doctor Robert Andrews Millikan for his work on the elementary charge of electricity and on the photoelectric effect.

We speak of an electric charge when electricity is accumulated on a body, and of an electric current when it spreads along a metallic wire. But when electricity passes through water or water solutions there is no current in the same sense of the word; there is a convection of charges combined with chemical decomposition - electrolysis. Thus water is decomposed into its constituents, hydrogen and oxygen, and metallic silver is deposited from solutions of silver salts. If one and the same current is used to cause these decompositions, the weight of hydrogen liberated in a certain time bears the same ratio to the weight of silver deposited as the atomic weight of hydrogen to the atomic weight of silver, and a current of a given strength in a given time always causes the appearance of a constant quantity of hydrogen and the depositing of a corresponding quantity of silver. As the strength of the current indicates the quantity of electricity passing through the fluids in a given time, it follows that the hydrogen atom and the silver atom carry the same charge, and this charge is what is meant by the unit of electric charge. The same laws hold good for all electrolytic processes, different atoms carrying as many units as are indicated by their valency. The charged atoms are called ions, but this word is used also in a wider signification.

It follows from these laws of electrolysis that it was possible to calculate the unit of electric charge with the same degree of probability with which the number of atoms in a gram of hydrogen could be estimated, and as early as **1874** an approximate value of the unit was arrived at in this way, equalling about two thirds of the exact value now known through the researches of Millikan. The word electron was proposed later as a name for the unit of charge, but now that the discovery of cathode rays has brought to our knowledge free units of negative electricity, an electron means an amount of negative electricity equalling the unit of charge.

Electricity does not pass through gases under normal conditions, but when a gas is exposed to X-rays it acquires the power of transmitting a current. It was soon proved that under the influence of these rays, positive and negative ions are formed, conveying charges of electricity in the same way as in the case of electrolysis. The discovery of radioactive elements provided still more powerful means for such an ionization of gases.

With the methods that were now available it could be shown that the unit of charge of the gas ions was approximately the same as the unit known from electrolysis. Ionization was also observed in monatomic inert gases, which proves that the unit of electric charge is a constituent of the atom that is liberated from it by ionization. Eager attempts were now made to obtain a more exact value for the unit of charge, but the results were not much better than before - until Millikan took up the problem.

Millikan's aim was to prove that electricity really has the atomic structure, which, on the base of theoretical evidence, it was supposed to have. To prove this it was necessary to ascertain, not only that electricity, from whatever source it may come, always appears as a unit of charge or as an exact multiple of units, but also that the unit is not a statistical mean, as, for instance, has of late been shown to be the case with atomic weights. In other words it was necessary to measure the charge of a single ion with such a degree of accuracy as would enable him to ascertain that this charge is always the same, and it was necessary to furnish the same proofs in the case of free electrons. By a brilliant method of investigation and by extraordinarily exact experimental technique Millikan reached his goal.

In his fundamental experiments he had two horizontal metal plates, one a short distance above the other, and by means of a switch he could join them with the poles of a source of high-tension current or short-circuit them. The air between the plates was ionized by radium that could be screened off. There was a minute pin-hole in the middle of the top plate, and over it he had arranged a spray of oil droplets with a radius of about one thousandth of a millimeter. Sooner or later such an oil droplet must fall through the pin-hole and enter the space between the plates, where it was illuminated in such a way that Millikan could see it in a telescope like a bright *star* on a black background. In the eyepiece of this telescope were placed three cross-hairs, and Millikan measured the time which the droplet required to pass between them. In this way he measured the velocity of fall, which for such small droplets is only a fraction of a millimeter a second. The droplet had been charged with electricity by the frictional process involved in blow-

ing the spray, and when it had fallen down, Millikan switched on the source of current so as to cause the drop to be pulled up by the attraction of the upper plate. The droplet rose, and its velocity was measured during its rise; then the plates were short-circuited, and the drop turned again and began to fall. In this way he kept the drop travelling up and down, many times during several hours, and measured its velocity again and again by means of a stop-watch or, later, a chronoscope. The velocity of fall was constant, but on the way up the velocity varied, which means that the drop had captured one or more of the ions spread in the air between the plates. Now in this experiment the difference of velocity is proportional to the charge captured, and the results showed that the difference of velocity always had the same value or an exact multiple of that value. In other words: the drop had caught one or more units of electrical charge, all exactly equal, however the experiments were varied. In this way the charge of a single ion could be measured in a very large number of cases, and it was determined with an exactitude of one in a thousand.

When the source of current is switched on, the positive ions are driven with a high speed towards the negative plate, and vice versa. Thus Millikan only needed to have the droplet near one of the plates at the moment when he switched on the source of current, if he wished to expose it to a shower of positive or negative ions and in this way alter its charge. By this method he proved that the electric charge which the drop had acquired by friction was an exact multiple of the unit.

To give unimpeachable proof Millikan was obliged to make similar experiments with cathode rays and with alpha- and beta-rays and, moreover, to investigate the law of fall of small bodies through gases and the law of their Brownian movements.

Even leaving out of consideration the fact that Millikan has proved by these researches that electricity consists of equal units, his exact evaluation of the unit has done physics an inestimable service, as it enables us to calculate with a higher degree of exactitude a large number of the most important physical constants.

In justifying the reward of Millikan the Academy has not omitted to refer also to his investigations of photoelectric effect. Without going into details I will only state that, if these researches of Millikan had given a different result, the law of Einstein would have been without value, and the theory of Bohr without support. After Millikan's results both were awarded a Nobel Prize for Physics last year.

ROBERT A. MILLIKAN

The electron and the light-quant from the experimental point of view

Nobel Lecture, May 23, 1924

The fact that Science walks forward on two feet, namely theory and experiment, is nowhere better illustrated than in the two fields for slight contributions to which you have done me the great honour of awarding me the Nobel Prize in Physics for the year 1923.

Sometimes it is one foot which is put forward first, sometimes the other, but continuous progress is only made by the use of both - by theorizing and then testing, or by finding new relations in the process of experimenting and then bringing the theoretical foot up and pushing it on beyond, and so on in unending alternations.

The terms of this year's award state that it is given for work on the fundamental electrical unit and on photoelectricity. In both fields my own work has been that of the mere experimentalist whose main motive has been to devise, if possible, certain crucial experiments for testing the validity or invalidity of conceptions advanced by others.

The conception of electrical particles or atoms goes back a hundred and seventy years to Benjamin Franklin who wrote about 1750: ((The electrical matter consists of particles extremely subtle since it can permeate common matter, even the densest, with such freedom and ease as not to receive any appreciable resistance.))

This theoretical conception was developed in no little detail by Wilhelm Weber¹ in papers written in **1871**. The numerical value of the ultimate electrical unit was first definitely estimated by G. Johnstone Stoney² in 1881, and in 1891 this same physicist gave to it the name *the electron**.

* It is highly desirable that this historically correct, etymologically most suitable, and authoritatively recognized nomenclature (see among many others Rutherford's Presidential Addresses at the British Association 1923, Nemst's Theoretical Chemistry, last edition, etc., etc.) be retained. When used without a prefix or qualifying adjective, the word electron may signify, if we wish, as it does in common usage, both the generic thing, the unit charge, and also the negative member of the species, precisely as the word « man » in English denotes both the genus homo and the male of mankind. There is no gain in convenience in replacing *positive electron, by «**proton**», but on the other hand a distinct loss logically, etymologically, and historically.

In 1897 the experimental foot came forward with J. J. Thomson's and Zeeman's determinations of e/m by two wholly distinct methods. It was these experiments and others like them which in a few years gained nearly universal acceptance among physicists for the electron theory.

There remained, however, some doubters, even among those of scientific credentials, for at least two decades - men who adopted the view that the apparent unitary character of electricity was but a statistical phenomenon; and as for educated people of the non-scientific sort, there exists today among them a very general and a very serious misconception as to the character of the present evidence. A prominent literary writer recently spoke of the electron as « only the latest scientific hypothesis which will in its turn give way to the abra-ca-da-bra of tomorrow ».

It is perhaps not inappropriate then to attempt to review today as precisely as possible a few features of the existing experimental situation and to endeavour to distinguish as sharply as may be between theory and some newly established facts.

The most direct and unambiguous proof of the existence of the electron will probably be generally admitted to be found in an experiment which for convenience I will call the oil-drop experiment. But before discussing the significance of that advance I must ask you to bear with me while I give the experimental answer to the very fundamental but very familiar query: « What is electricity? » His answer is naive, but simple and definite. He admits at once that as to the *ultimate* nature of electricity he knows nothing.

He begins rather with a few simple and familiar experiments and then sets up some definitions which are only descriptions of the experiments and therefore involve no hypothetical elements at all.

He first notes the fact that a pith ball, after contact with a glass rod that has been rubbed with silk, is found to be endowed with the new and striking property that it tends to move away from the rod with a surprisingly strong and easily measurable force. He describes that fact, and affirms at the same time his ignorance of all save the existence of this force, by inventing a new word and saying that the pith ball has been put into a *positively electrified state*, or simply has received a *charge of positive electricity*. He then measures the amount of its charge by the strength of the observed force.

Similarly he finds that the pith ball, after contact with an ebonite rod that has been rubbed with cat's fur is attracted, and he proceeds to describe this experiment by saying that it has now received a *charge of negative electricity*. Whenever the pith ball is found to have been put, by contact with any body

or by any other process, into a condition to behave in either of the foregoing ways, it has, by *definition*, received a charge of either positive or negative electricity. The whole of our thinking about electrical matters starts with these two simple experiments and these two definitions.

In order now to get the most crucial possible test of the correctness or incorrectness of Franklin's conception of a particle, or an atom, of electricity it was clearly necessary to reduce the charge on the pith ball to the smallest possible amount, to change that charge by the most minute possible steps, and then to see whether the forces acting upon it at a given distance from the glass rod (i.e. in a constant field) had any tendency to increase or decrease by *unitary* steps.

The success of the experiments first performed in 1909, was *wholly* due to the design of the apparatus, i.e. to the relation of the parts.

The pith ball itself which was to take on the smallest possible charge had of course to be the smallest spherical body which could be found and yet which would remain of constant mass; for a continuously changing gravitational force would be indistinguishable, in its effect upon the motion of the charged body, from a continuously changing electrical charge.

A non-homogeneous or non-spherical body also could not be tolerated; for the force acting on the pith ball had to be measured by the speed of motion imparted to it by the field, and this force could not be computed from the speed unless the shape was spherical and the density absolutely constant. This is why the body chosen to replace the pith ball was an individual oil-droplet about a thousandth of a millimeter in diameter blown out of an ordinary atomizer and kept in an atmosphere from which convection currents had been completely removed by suitable thermostatic arrangements. The glass rod, the purpose of which was to produce a constant electrical field, was of course replaced by the two metal plates C and D (Fig. 1) of an air condenser, one of the plates (D) being attached to the positive, the

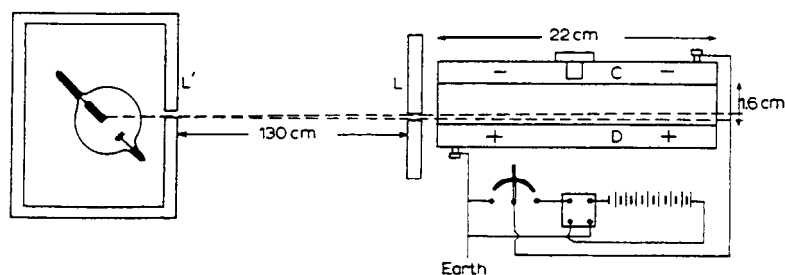


Fig. 1.

other (C) to the negative terminal of a battery, and a switch being added, as shown in the figure, so as to make it possible to throw the field on or off at will.

In order to be able to measure very accurately the force acting upon the charged oil-droplet it was necessary to give it about a centimeter of path in which the speed could be measured. This is one of the most important elements in the design, the overlooking of which has caused some subsequent observers to fall into error. The centimeter of path and the constancy of field then fixed the approximate size of the plates the diameter of which was actually 22 cm. They were placed 16 mm apart.

The field strength too, about 6,000 volts per cm, was vital, and new in work of anything like this kind. It was the element which turned possible failure into success. Indeed, Nature here was very kind. She left only a narrow range of field strengths within which such experiments as these are all possible. They demand that the droplets be large enough so that the Brownian movements are nearly negligible, that they be round and homogeneous, light and non-evaporable, that the distance be long enough to make the timing accurate, and that the field be strong enough to more than balance gravity by its pull on a drop carrying but one or two electrons. Scarcely any other combination of dimensions, field strengths and materials, could have

Table 1.

<i>Time of fall 1.303 cm under gravity (sec)</i>	<i>Time of rise 1.303 cm in field (sec)</i>	<i>Mean times of rise in field (sec)</i>	<i>Divisors for speeds due to field</i>	<i>The elec- tron in terms of a speed</i>
120.8	26.2			
121.0	11.9			
121.2	16.5	67.73	1	3.007
120.1	16.3	26.40	2	3.009
120.2	26.4	16.50	3	2.993
119.8	67.4	11.90	4	3.008
120.1	26.6			
—	16.6			
120.2	16.6	<i>Mean time</i>		
—	16.4	<i>of fall under</i>		
120.2	68.0	<i>gravity</i>		
119.9	67.8	120.35		
—	26.4			

yielded the results obtained. Had the electronic charge been one-tenth its actual size, or the sparking potential in air a tenth of what it is, *no* such experimental facts as are here presented would ever have been seen.

The observations which gave an unambiguous answer to the questions as to the atomic nature of electricity consisted in putting a charge upon the drop, in general by the frictional process involved in blowing the spray, letting the charged drop drift through a pin-hole in the center of plate C into the space between C and D, and then in changing its charge in a considerable number of different ways; for example, by ionizing the air just beneath it by alpha, beta, or gamma rays from radium and letting the field throw these ions into the drop; by illuminating the surface of the drop itself with ultraviolet light; by shooting X-rays both directly at it and beneath it, etc. The results of those changes in charge in a constant field, as is now well-known, and as is shown in particular cases in the accompanying Table 1, were

(1) that it was found possible to discharge the droplet completely so that within the limits of observational error-a small fraction of one per cent - *it fell its centimeter undergravity, when the 6,000 volt electrical-field was on, in precisely the same time required to fall the same distance when there was no field;*

(2) that it could become endowed with a particular speed in the electrical field (corresponding to 67.7 sec in the particular case shown), which *could be reproduced as often as desired, but which was the smallest speed that the given field ever communicated to it* - nor was this change in speed due to the capture of an electron a small one, difficult to observe and measure. It was often larger than the speed due to gravity itself and represented, as in this case shown, a reversal *in direction* so that it was striking and unmistakable;

(3) that *speeds exactly two times, three times, four times, five times, etc.* (always within the limits of observational error - still less than a percent) *could be communicated to the droplet, but never any fraction of these speeds.*

He who has seen that experiment, and hundreds of investigators have observed it, has literally *seen* the electron. For he has measured (in terms of a speed) the smallest of the electrical forces which a given electrical field ever exerts upon the pith ball with which he is working and with the aid of whose movements he defines electricity itself. Further, he has found that that something which he has chosen to call electricity may be placed upon or removed from his pith ball only in quantities which cause the force acting upon it either to drop to zero, or else to go up by definite integral multiples of the smallest observed force.

If a man had seen a football which someone told him was the electron he would be far less certain that what he had seen corresponded to reality, than 'is the man who has become familiar with the foregoing experiment. By its aid he can count the number of electrons in a given small electrical charge with exactly as much certainty as he can attain in counting his fingers and his toes. It is true that when he has counted up to 200 electrons in a given charge, his observational error begins to make it impossible to distinguish between 200 and 201; so that the conclusion that large electrical charges are built up in the same manner as are the charges that he can count is of course in the nature of a generalization, but obviously not one of much uncertainty.

But the electron itself, which man has measured, as in the case shown in the table, is neither an uncertainty nor an hypothesis. It is a new experimental fact that this generation in which we live has for the first time seen, but which anyone who wills may henceforth see.

The measurement of the electron, not as above in terms of the speed that it imparts to a given oil-drop, but in absolute electrostatic units, involved observations of the foregoing sort upon thousands of drops of various sizes, made from a number of different substances, surrounded by a large number of different gases at widely differing pressures, varying from atmospheric down to a millimeter and a half of mercury.

It involved also years of work in finding accurate values of gaseous viscosities, and in determining just how « Stokes' law » must be modified to yield the complete law of fall of a particle through a gas at any density whatever.

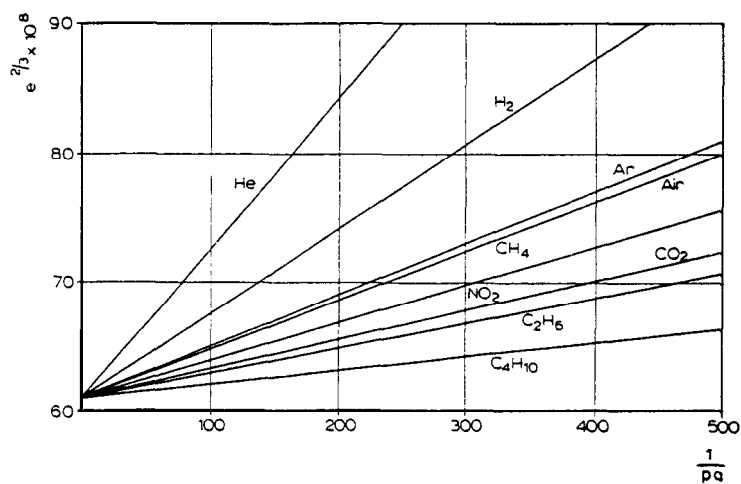


Fig. 2.

But all this is only of interest here in showing, as Fig. 2 does*, *how inevitably all observations on all gases and all substances converge upon the same absolute value of the electron at the intercept on the $e^{\frac{1}{2}}$ axis of the figure.* It is from this intercept that the value of the electron $e = 4.774 (\pm 0.005) \times 10^{-10}$ absolute electrostatic units is directly obtained.

After ten years of work in other laboratories in checking the methods and the results obtained in connection with the oil-drop investigation published from 1909 to 1923, there is practically universal concurrence upon their correctness, despite the vigorous gauntlet of criticism which they have had to run.

Electrons, of both the positive and negative variety, are then merely observed centers of electrical force, just as was the charged pith ball from which we got our original definition of an electric charge, the difference being that electrons are invariable in their charge while pith-ball charges are built up out of them.

The dimensions of electrons may in general be ignored; i.e. they may both, for practical purposes, be considered as point charges, though, as is well known, the positive has a mass 1,845 times that of the negative. Why this is so no one knows. It is another experimental fact.

It is also well-known that we can now count the exact number of positives and of negatives in every atom; that we can locate all the positives in the nucleus; that we find the negatives scattered partly through the outer regions and partly held within the nucleus; that the number of outer negatives varies from 1 in hydrogen by unit steps up to 92 in uranium, and that the number of negatives in the nucleus is given by the difference between the atomic weight and the atomic number.

Shall we ever find that either positive or negative electrons are divisible? Again no one knows; but we can draw some inferences from the history of the chemical atom. This is sometimes said by the unthinking to have exploded, but of course every scientist knows that it has never lost an iota of its old reality nor of its old vitality. From an experimental point of view the atom of the chemist was all contained in the facts of definite and multiple proportions in combining powers. For the purposes for which the concept was used, viz. those of chemical combination, the chemical atom is just as much the ultimate unit now as it ever has been.

* This is taken from a repetition of my observations in different gases by my assistant Dr. Yoshio Ishida. For similar observations upon different drop-substances, see *The Electron*, rev. ed., University of Chicago Press, 1924.

Similarly it is not likely that the field in which the electron has already been found to be the unit, namely that of atomic structure, will ever have to seek another unit. The new *facts* which this generation has discovered are certainly the permanent heritage of the race. If the electron is ever subdivided it will probably be because man, with new agencies as unlike X-rays and radioactivity as these are unlike chemical forces, opens up still another field where electrons may be split up without losing any of the unitary properties which they have now been found to possess in the relationships in which we have thus far studied them.

The second domain in which, as your award indicates, I have been attempting to take another step, and to assist in bringing the experimental foot up to parallelism at least with the theoretical, is the field of ether waves. In this domain I have been seeking since the year 1904 to find some crucial test for the Thomson-Planck-Einstein conception of localized radiant energy.

This conception in its most general form was introduced by J. J. Thomsons in 1903 to account for two newly discovered experimental facts, viz. :

(1) that X-rays pass over all but an exceedingly minute fraction, say one in a billion, of the atoms contained in the space traversed without spending any energy upon them, but here and there find an atom from which they hurl an electron with enormous speed;

(2) that ultraviolet light has the amazing property, discovered by Lenard⁴ in 1902, of ejecting electrons from metal surfaces with an energy which is independent of the intensity of the source.

This Thomson semicorpuscular conception of localized radiant energy was taken up in 1905 by Einsteins who, by combining it with the facts of quanta discovered by Planck⁶ through his analysis of black-body radiation, obtained an equation which should govern, from his viewpoint, the interchange of energy between ether waves and electrons, viz. $\frac{1}{2}mv^2 = h\nu - P$, the first term representing the energy with which the electron escapes, the second term Planck's energy quantum for the particular light employed, and the last the work necessary to get the electron out of the metal.

After ten years of testing and changing and learning and sometimes blundering, all efforts being directed from the first toward the accurate experimental measurement of the energies of emission of photoelectrons, now as a function of temperature, now of wavelength, now of material (contact e.m.f. relations), this work resulted, contrary to my own expectation, in the first direct experimental proof⁷ in 1914 of the exact validity, within

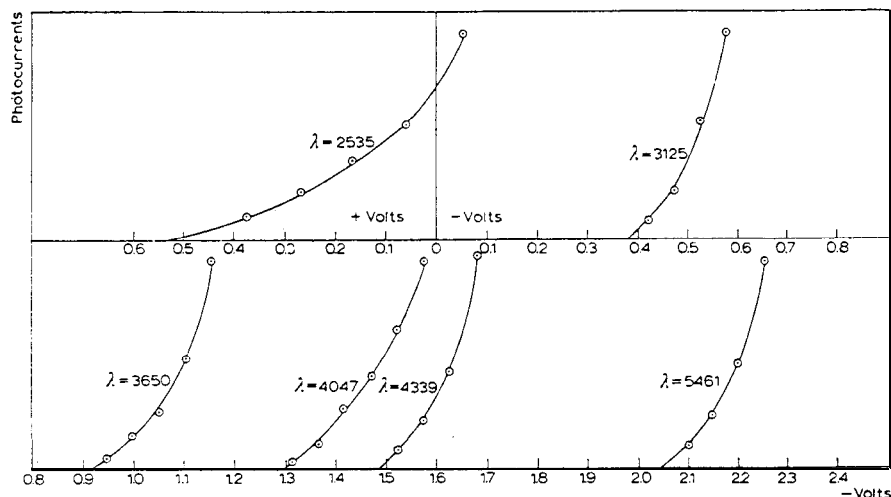


Fig. 3.

narrow limits of experimental error, of the Einstein equation, and the first direct photoelectric determination of Planck's h . The accuracy obtained was about 0.5% which was much the best available at the time. Figs. 3 and 4, which represent the most accurate work done on an individual metal (sodium), will illustrate the entire lack of ambiguity of the result.

This work, like that on the electron, has had to run the gauntlet of severe criticism, for up to 1916 not only was discussion active as to whether there were any limiting velocity of emission, but other observers who had thought that a linear relation existed between energy and frequency had not found the invariable constant h appearing as the ratio. But at the present time it is not too much to say, that the altogether overwhelming proof furnished by the experiments of many different observers, working by different methods in many different laboratories, that Einstein's equation is one of exact validity (always within the present small limits of experimental error) and of very general applicability, is perhaps the most conspicuous achievement of Experimental Physics during the past decade.

A brief historical summary of this advance is as follows: A year or two after the foregoing photoelectric work was completed, Duane⁸ and his associates found unambiguous proof of a relation which is just the inverse of Einstein's. They bombarded a metal target with electrons of known and constant energy and found that the maximum frequency of the ether waves (general X-radiation) thereby excited was given, with much precision, by $\frac{1}{2}mv^2 = hr$.

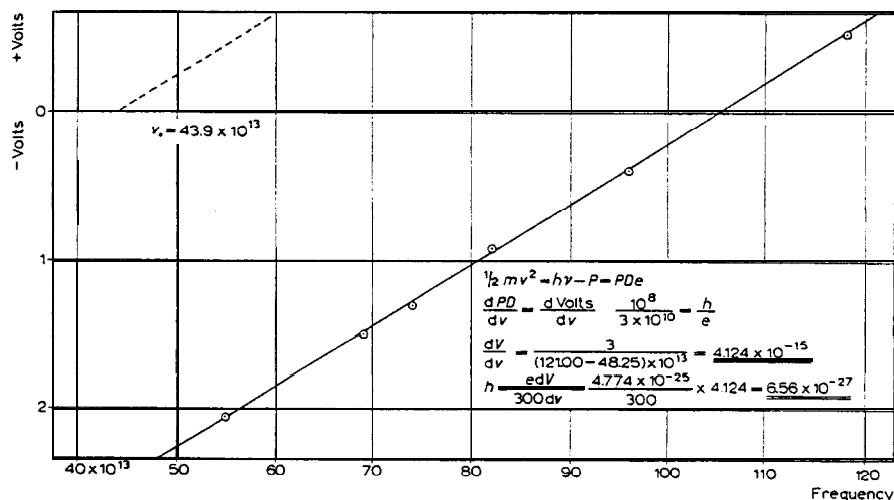


Fig. 4.

D. L. Webster⁹ then proved that the characteristic X-ray frequencies of atoms begin to be excited at just the potential at which the energy of the stream of electrons which is bombarding the atoms has reached the value given by $h\nu = \frac{1}{2}mv^2$ in which ν is now the frequency of an absorption edge.

De Broglie¹⁰ and Ellis¹¹, on the other hand, measured with great precision the speed of electrons ejected from different atomic levels by high-frequency radiations and thus beautifully verified, in this high-frequency field, precisely the same Einstein equation $\frac{1}{2}mv^2 = h\nu - P$ which I had found to hold for ultraviolet and visible frequencies.

Parallel with these developments has come the very full working out of the large field of ionizing and radiating potentials. This has also involved the utilization and verification of the same reciprocal relation between frequency and electronic energy which is stated in the Einstein equation and which constitutes in its inverse form the cornerstone of Bohr's epoch-making treatment of spectral lines. This work all takes its start in Franck and Hertz' fundamental experiment⁺, but the field has been most actively and successfully explored since 1916 in America, especially by Foote and Mohler, Wood, Davis and Goucher, McLennan, and others¹³.

In view of all these methods and experiments the general validity of Einstein's equation is, I think, now universally conceded, and *to that extent the reality of Einstein's light-quanta may be considered as experimentally established*. But the conception of *localized* light-quanta out of which Einstein got his equation must still be regarded as far from being established. Whether the

mechanism of interaction between ether waves and electrons has its seat in the unknown conditions and laws existing within the atom, or is to be looked for primarily in the essentially corpuscular Thomson-Planck-Einstein conception as to the nature of radiant energy is the all-absorbing uncertainty upon the frontiers of modern Physics.

In 1921¹⁴ I thought I had taken another step toward its solution in proving that in the photoelectric process the light energy $h\nu$ is taken up, not only by electrons within atoms, but also by the free (i.e. the conduction) electrons in metals. For this seemed to take the absorbing mechanism out of the atom entirely and to make the property of imparting the energy $h\nu$ to an electron, whether free or bound, an intrinsic property of light itself.

But a beautiful discovery by Klein and Rosseland¹⁵ a year later in Bohr's Institute made this conclusion unnecessary. For it showed, as Dr. Epstein first pointed out, that there was an intermediate process, namely a collision of the second kind, by which the energy might be transferred, without loss, *indirectly* from the light wave to the conduction electron, thus obviating the necessity of a direct transfer. The act of absorption could still, then, be an atomic process and the absorbed energy be afterward passed on by a collision of the second kind to a free electron. This important discovery then left the evidence for localized light-quanta just where it was before.

Within the past year, however, a young American physicist, Arthur H. Compton¹⁶ of the University of Chicago, by using the conception of localized light-quanta, has brought forward another new phenomenon which at least shows the fecundity of the Einstein hypothesis. Compton goes a step farther than Einstein in that he assumes not only the existence of light-quanta but also that in the impact between a light-quant and a free electron the laws of conservation of energy and of conservation of momentum both hold. This assumption enables him to compute exactly how much the frequency of ether waves which have collided with free electrons will be lowered because of the energy which they have given up to the electron in the act of collision, and therefore the loss which their own $h\nu$ has experienced. He then finds experimentally that there is approximately the computed lowering in frequency when monochromatic X-rays from molybdenum are scattered by carbon. Further Ross¹⁷ at Stanford University has checked this result by the photographic method.

On account of the fact that Duane and his co-workers at Harvard University could not find a trace of the Compton effect, Messrs. Becker¹⁸, Watson, and Smythe have within a month, at the California Institute at Pasadena,

repeated the same type of scattering experiments as those made by Ross, using however aluminium as a scatterer, and *have found on one plate, taken with high resolution, the alpha doublet line of molybdenum shifted as a clearly observable doublet toward longer wavelengths*. Further the amount of the shift was here measurable with an accuracy of about 1% and agreed within this narrow limit with that predicted by Compton's equations. Fig. 5 shows one of these

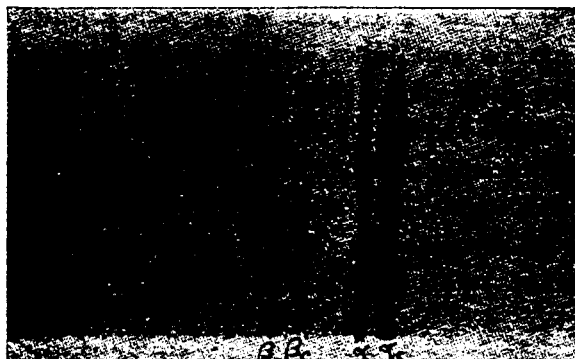


Fig. 5.

new photographs in which both the α and β lines of molybdenum are shifted toward longer wavelengths the correct amount, i.e. to α_c and β_c , through being scattered by aluminium. It may be said then without hesitation that it is not merely the Einstein equation which is having extraordinary success at the moment, but the Einstein conception as well.

But until it can account for the facts of interference and the other effects which have seemed thus far to be irreconcilable with it, we must withhold our full assent. Possibly the recent steps taken by Duane¹⁹, Compton²⁰, Epstein and Ehrenfest²¹ may ultimately bear fruit in bringing even interference under the control of localized light-quanta. But as yet the path is dark.

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Biography

Robert Andrews Millikan was born on the 22nd of March, 1868, in Morrison, Ill. (U.S.A.), as the second son of the Reverend Silas Franklin Millikan and Mary Jane Andrews. His grandparents were of the Old New England stock which had come to America before 1750, and were pioneer settlers in the Middle West. He led a rural existence in childhood, attending the Maquoketa High School (Iowa). After working for a short time as a court reporter, he entered Oberlin College (Ohio) in 1886. During his undergraduate course his favourite subjects were Greek and mathematics; but after his graduation in 1891 he took, for two years, a teaching post in elementary physics. It was during this period that he developed his interest in the subject in which he was later to excel. In 1893, after obtaining his mastership in physics, he was appointed Fellow in Physics at Columbia University. He afterwards received his Ph.D. (1895) for research on the polarization of light emitted by incandescent surfaces-using for this purpose molten gold and silver at the U.S. Mint.

On the instigation of his professors, Millikan spent a year (1895-1896) in Germany, at the Universities of Berlin and Göttingen. He returned at the invitation of A. A. Michelson, to become assistant at the newly established Ryerson Laboratory at the University of Chicago (1896). Millikan was an eminent teacher, and passing through the customary grades he became professor at that university in 1910, a post which he retained till 1921. During his early years at Chicago he spent much time preparing textbooks and simplifying the teaching of physics. He was author or co-author of the following books: *A College Course in Physics*, with S. W. Stratton (1898) ; *Mechanics, Molecular Physics, and Heat* (1902) ; *The Theory of Optics*, with C. R. Mann-translated from the German (1903); *A First Course in Physics*, with H. G. Gale (1906) ; *A Laboratory Course in Physics for Secondary Schools*, with H. G. Gale (1907); *Electricity, Sound, and Light*, with J. Mills (1908); *Practical Physics*-revision of *A First Course* (1920) ; *The Electron* (1917; rev. eds. 1924, 1935).

As a scientist, Millikan made numerous momentous discoveries, chiefly in the fields of electricity, optics, and molecular physics. His earliest major suc-

cess was the accurate determination of the charge carried by an electron, using the elegant ((falling-drop method)) ; he also proved that this quantity was a constant for all electrons (1910), thus demonstrating the atomic structure of electricity. Next, he verified experimentally Einstein's all-important photoelectric equation, and made the first direct photoelectric determination of Planck's constant h (1912-1915). In addition his studies of the Brownian movements in gases put an end to all opposition to the atomic and kinetic theories of matter. During 1920-1923, Millikan occupied himself with work concerning the hot-spark spectroscopy of the elements (which explored the region of the spectrum between the ultraviolet and X-radiation), thereby extending the ultraviolet spectrum downwards far beyond the then known limit. The discovery of his law of motion of a particle falling towards the earth after entering the earth's atmosphere, together with his other investigations on electrical phenomena, ultimately led him to his significant studies of cosmic radiation (particularly with ionization chambers).

Throughout his life Millikan remained a prolific author, making numerous contributions to scientific journals. He was not only a foremost scientist, but his religious and philosophic nature was evident from his lectures on the reconciliation of science and religion, and from his books : *Science and Life* (1924) ; *Evolution in Science and Religion* (1927); *Science and the New Civilization* (1930); *Time, Matter, and Values* (1932). Shortly before his death he published *Electrons (+ and -), Protons, Photons, Neutrons, Mesotrons, and Cosmic Rays* (1947; another rev. ed. of *The Electron*, previously mentioned,) and his *Autobiography* (1950).

During World War I, Millikan was Vice-Chairman of the National Research Council, playing a major part in developing anti-submarine and meteorological devices. In 1921, he was appointed Director of the Norman Bridge Laboratory of Physics at the California Institute of Technology, Pasadena; he was also made Chairman of the Executive Council of that institute. In 1946 he retired from this post. Professor Millikan has been President of the American Physical Society, Vice-President of the American Association for the Advancement of Science, and was the American member of the Committee on Intellectual Cooperation of the League of Nations, and the American representative at the International Congress of Physics, known as the Solvay Congress, at Brussels in 1921. He held honorary doctor's degrees of some twenty-five universities, and was a member or honorary member of many learned institutions in his country and abroad. He has been the recipient of the Comstock Prize of the National Academy of Sciences, of the

Edison Medal of the American Institute of Electrical Engineers, of the Hughes Medal of the Royal Society of Great Britain, and of the Nobel Prize for Physics 1923. He was also made Commander of the Legion of Honour, and received the Chinese Order of Jade.

Millikan was an enthusiastic tennis player, and golf was also one of his recreations.

Professor Millikan married Greta Erwin Blanchard in 1902; they had three sons: Clark Blanchard, Glenn Allen, and Max Franklin.

He died on the 19th of December, 1953, in San Marino, California.

Physics 1924

KARL MANNE GEORG SIEGBAHN

((for his discoveries and research in the field of X-ray spectroscopy))

Physics 1924

*Presentation Speech by Professor A. Gullstrand, Chairman of the Nobel Committee
for Physics of the Royal Swedish Academy of Sciences*

Your Majesty, Your Royal Highnesses, Ladies and Gentlemen.

The Royal Academy of Sciences has this year awarded the Nobel Prize for Physics for 1924 to Karl Manne Georg Siegbahn, Professor at the University of Uppsala, for his discoveries and researches in X-ray spectroscopy.

When the Prize for Physics was awarded to Röntgen at the First Nobel Festival, the conception of a spectrum of X-rays could not be set up, or at least could not be supported by experimental evidence. In fact, the domain of the work for which a prize has now been awarded did not yet exist. The assumption that X-radiation, like the radiation long known under the names of light and heat, consisted of transverse electric oscillations, it is true, was advanced by eminent scientists at a comparatively early date; but every attempt to demonstrate any of the phenomena characteristic of such oscillations - such as refraction, polarization or diffraction and interference - yielded results that were negative, or at least not free from ambiguity. The only means of distinguishing different kinds of X-rays was, and remained until later, the penetrative power or what is known as the degree of hardness, which was accessible for physical measurement.

But in the hands of a skilful investigator even this means was sufficient for the discovery of the characteristic X-radiation of the elements. Barkla in Edinburgh found that a series of elements, independently of the chemical composition in which they were used, emitted, in a certain experiment, X-rays of a degree of hardness which was characteristic of the element in question. As he proceeded from element to element with increasing atomic weight, the penetrative power of the characteristic radiation became greater, in other words the X-rays became harder and harder. If the atomic weight was sufficiently high, there appeared a new and much softer characteristic radiation, which in the same way became more and more penetrating the higher the atomic weight possessed by the element investigated. Barkla called these two radiations, by means of which the different elements could thus be distinguished from one another, their K- and L-radiation. These fundamental

discoveries, as was soon to be seen, belong already to the domain of X-ray spectroscopy.

After Barkla had also found a kind of polarization of X-rays, it became more and more probable - though this phenomenon did not appear in the same way as the polarization of light - that the two forms of radiation were after all of the same nature, and enough progress had been made to render it possible to estimate the order of magnitude of the wavelength of the X-radiation, if that radiation really were a wave motion.

A spectrum in which every place corresponds to a definite wavelength is obtained by decomposing composite light. If all wavelengths are represented in this light, the spectrum is continuous; if not, the spectrum consists of lines or bands. The decomposition into a spectrum is effected either by refraction in a prism or by diffraction and interference in a grating. As gratings, there are generally used parallel grooves, very close together in a reflecting metal surface, but also gratings that let the light through, decompose it, in which case a spectrum may result both by the passage of the light and by its reflection. The closer together the grooves are, the more effective is the decomposition and the shorter are the wavelengths that can be investigated. Metal gratings have been employed with great success for the investigation of wavelengths of that order of magnitude that occurs in light; but there seemed to be no prospect of measuring by such means the wavelengths, several thousand times smaller, which, it was estimated, should characterize X-radiation. If, on the other hand, as was assumed in crystallography, a regular arrangement of the atoms or the molecules in a space lattice was the basis of the shapes of the natural crystals, then, according to estimates, the distances of the points of the lattice ought to be exactly of that order of magnitude that was required for the decomposition of X-radiation in a spectrum. If this radiation were essentially a wave motion, therefore, a crystal ought to be a suitable grating for the spectral decomposition of the radiation, whether the X-rays had passed through the crystal or had been reflected in it. But it was only von Laue who drew from this the conclusion that an inquiry ought to be made as to whether such a diffraction and interference could be shown photographically when the X-rays passed through crystals. The experiment showed that this was the case. This epoch-making discovery, which not only bore upon the nature of X-radiation and the reality of the space lattice assumed in crystallography, but also placed a new means of research into the hands of Science, was rewarded with the Nobel Prize for 1914, though its distribution was postponed till the following year.

The new phenomenon could be employed for two different purposes, both for investigations of the crystal lattices and for spectral investigation of the X-radiation itself. It was only natural that precedence was given to the investigations first named, as a fruitful spectroscopical investigation of X-rays presupposed a certain knowledge of the lattice used. Inasmuch as this is a three-dimensional grating, its effect is in essential respects unlike the effect of the previously known line and cross gratings. It was by a stroke, brilliant in its simplicity, that the Englishman W. L. Bragg succeeded in replacing von Laue's comparatively complicated theory of the effect of the crystal lattice by an extremely manageable formula, which could not only be employed to interpret von Laue's photographs obtained by X-rays passing through the crystals, but also enabled his father, W. H. Bragg, to design a real X-ray spectrometer, which was based, like the majority of subsequent designs, on the reflection of radiation. With these means father and son cooperated in investigating the often very complicated structure of the lattices in a number of crystals; and their services were rewarded with the Nobel Prize for Physics of 1915.

The second path through the newly discovered region of X-ray spectroscopy, namely the investigation of X-radiation in the different elements, was trodden with the greatest success by the young scientist Moseley, who was also an Englishman. As the penetrative power of X-radiation increases with the decrease of the wavelength, it was now evident that Barkla's K- and L-rays must represent more or less limited X-ray spectra, which in passing over to elements with a higher atomic weight are displaced in the direction of shorter wavelengths. Now, Moseley investigated these rays by a photographic method and found the former to consist of two, the latter of four, spectral lines. He further discovered the simple mathematical law by means of which the frequencies determined by the position of the lines - and consequently the corresponding wavelengths - can be obtained by what is known as the atomic number, i.e. the number of the element in a series in which all the elements are arranged with a generally increasing atomic weight. As the atomic number has proved to distinguish the elements better than the atomic weight, it has now attained the very greatest importance for atomic physics of the present day. Moseley fell at the Dardanelles before he could be awarded the prize, but his researches had directed attention to the merits of Barkla, who consequently in 1918 was proposed for the Nobel Prize, which was awarded to him without delay.

Siegbahn has won his place in this noble row of eminent investigators by

the work for which the Prize has now been awarded to him. It had already become clear that the X-radiation must arise in the inner parts of the atoms, and that consequently exact X-ray spectroscopical investigations form the only means for an experimental research of those parts. Clearly perceiving this fact, Siegbahn has in the course of ten years' assiduous and systematic labour devised a series of improvements and new designs dealing with almost every detail of the various apparatus and so constantly increased the exactitude of his measurements. The method has generally been photographic, and the crystal lattices have been used not only for reflection but also, in the case of shorter wavelengths, for diffraction of rays passing through the crystals. The high level to which he has brought X-ray spectroscopy can perhaps best be defined by the statement that the exactitude with which wavelengths can now be measured by his methods is a thousand times greater than that attained by Moseley. It was only to be expected that these much more accurate means would in his hand be used for a series of new discoveries. Thus to begin with, he has found a large number of new lines in the K- and L-series. Moreover he has made the experimental discovery of a new characteristic X-radiation, the M-series; and another such radiation, the N-series, has been discovered under his guidance. The fact that the existence of these radiations had already been surmised by Barkla in no wise diminishes the scientific value of their discovery and exact measurement.

In order to obtain an idea as to what has been gained by the researches of Siegbahn and his collaborators, it is sufficient to compare Moseley's results, two K-lines and four L- lines, with Siegbahn's statement ten years later. The K- series has been recently subjected to a fresh investigation for 42 elements. For 27 of these all the four main lines have been determined. For the lighter elements there are also special tables of eight fainter lines. The L- series has 28 lines and has been investigated for some 50 elements. The new M-series with 24 lines has been examined for 16 elements, and the N- series, which is also new, has been demonstrated for three of the heaviest elements, whereby five lines belonging to that series have been measured for uranium and thorium.

Siegbahn's work attains the character that is required for the award of the Nobel Prize not only because his methods of measurement provide an implement of hitherto undreamt-of exactitude, apt to further new scientific advances, or because he himself has used them to make a number of new discoveries, but above all owing to the importance for atomic physics that his methods of measurement and discoveries have.

It is obvious to everybody that it will always remain one of the chief goals

of physics to gain knowledge of the laws that regulate the energy relations within the atom and the exchange of energy between the atoms and the various forms of radiations. But that goal lay far away as long as no other radiations were known than the electromagnetic oscillations that appear in the form of light, dark heat radiation, or ultraviolet rays, and the analogous oscillations with wavelengths of a higher order of magnitude which are brought about directly by electricity, and which play such a great part in our days. So long as science was restricted to these means of research, there was no such thing as atomic physics. Scientists worked on the assumption that the oscillations were emitted by what are known as dipoles, consisting of two points, one charged with positive electricity and the other with negative electricity, which were bound to one another by an attractive force.

Then came the discovery of the corpuscular radiations, first the cathode rays which, in a sufficiently strong vacuum, proceed from the negative pole of a suitable source of electric current to the positive pole, and which consist of free negative electric units of charge, known as electrons, and then the discovery of radioactive radiation, which, together with an electron radiation and: an X-radiation of very short wavelength, contains positively charged corpuscles, known as alpha particles. With these means of research, it soon became evident that the notion of oscillating dipoles could not give a satisfactory picture of the structure of the atom.

Planck, however, even before a better picture had been obtained, had come to the conclusion that, if the electromagnetic theory is correct, it is impossible to obtain a theory of heat radiation agreeing with the facts without introducing the assumption that each dipole can exist only in a discontinuous series of different states of oscillation. The product of the frequency and a hitherto unknown constant, forms a value of energy, known as a quantum, and the dipoles can have no other values of energy than those which consist of an integral number of such quanta. The great importance due to this famous Planck's constant was only made clear through the later development of atomic physics.

A logical consequence of Planck's theory is that a transition from one state to another can only take place in such a way that an integral number of energy quanta is emitted or absorbed. An exchange of energy between matter and radiation, therefore-that is to say an emission or absorption of radiation-can be effected only by the transmission of an integral number of energy quanta. It was not Planck, however, but Einstein, that drew this conclusion, which involves the law of the photoelectric effect-a law that now,

especially thanks to Millikan's work, has been verified in a brilliant manner. It is through Einstein's law that the Planck's constant and the whole-quanta theory have attained their greatest importance.

After the electrons had been discovered, and after it had been found that their mass is in round numbers only a two-thousandth part of that of an atom of hydrogen- while the positive unit charge never appears with a mass of such a small order of magnitude - atom models were devised in accordance with this fact. An observation that Rutherford made in the investigation of the paths of alpha particles shot out from radioactive substances, showed that the positively charged parts of an atom must be very small in proportion to the whole atom. According to his view, therefore, the atom consisted of a positive nucleus, surrounded by electrons moving in orbits, in the same way as the sun is surrounded by its planets. Rutherford's atom model is the prototype of the one we now have, both in the matter of the distribution of electric charges and also in a much more important respect: it is in conflict with the electromagnetic theory of light.

The fact that this contradiction already existed and apparently could not be removed, provides perhaps a psychological explanation of the fact that someone hit upon the idea of propounding a theory like the one now accepted. It was the young Dane Bohr who carried things to a conclusion and laid down amongst his fundamental postulates that the electrons -in conflict with the current theory - do not radiate energy through their orbital motion. The electrons can only move in so-called stationary orbits, and energy is emitted or absorbed by the passing of an electron from one orbit to another. In accordance with Einstein's law, the exchange of energy between atom and radiation in such cases is always a quantum, forming the product of the frequency of the radiation with the Planck's constant, and the various stationary qualities that the atoms may possess are thus distinguished from one another by amounts of energy that form an integral number of Planck's quanta. This theory, which in the course of its development and accomplishment in the hands of a large number of investigators has attained a high degree of perfection, is supported experimentally by the fact that it is in accordance with important evidence concerning line spectra and the decomposition of spectral lines under the influence of magnetic and electric forces. For the merits thus indicated, both Planck and Einstein on the one hand, and also Bohr on the other, have been awarded the Nobel Prize for Physics.

As the chemical properties of the elements vary periodically with increasing atomic weight, while the characteristic X-radiation shifts continuously

from element to element throughout the whole series, regardless of the chemical composition in which the element is used in exciting the radiation, it can be concluded already from Barkla's researches that the X-radiation must arise in the inner parts of the atom. Moseley's researches show again that the atomic number discovered by him in Bohr's atomic theory must give the number of free positive unit charges in the nucleus of the atom, that is to say also the number of electrons that move in the orbits when the atom is electrically neutral. In an element that can emit both K- and L-rays, the former radiation has much shorter wavelengths and consequently greater frequencies than the latter. As the energy quanta are proportional to the frequencies, therefore, the K radiation involves a larger change in the energy of the atom than the L radiation; and in the atomic theory this is as much as to say that an orbit into which an electron falls on emission of a K-line must lie nearer the nucleus than an orbit to which an electron falls on emission of an L-line. In this way it was inferred that there is a K-level nearest the nucleus, outside that an L-level, and after that an M-level and an N-level, all these four being experimentally determined. Further out hypothetical O- and P-levels have been assumed in the atomic scheme.

It is only through a consideration of these results that the importance of the discovery of the M- and N-series is fully realized. The value of Siegbahn's exact measurements and discoveries of new lines is best illustrated by the fact that they have formed the foundation of the work of a number of investigators, through which it has become evident that there are three different L-levels of energy, five M-levels, seven N-levels, and so on. The results of his measurements, in fact, form an immense material which is as yet far from being fully worked out, and which for a long time to come will probably remain the touchstone for future modifications or revolutions in atomic physics.

To this account of the most outstanding features of Siegbahn's work it will suffice to add that, partly alone and partly in collaboration with his pupils, he has made a number of other discoveries in the same subject. These include, for instance, an apparatus with which it is possible, by means of two X-ray exposures each lasting two hours, to make a qualitative analysis of an unknown substance and thereby find out all the elements in the substance extending from sodium with the atomic number 11 to uranium with the atomic number 92. And finally, also the refraction of X-rays in a prism, hitherto sought for with no less zeal than futility, has been demonstrated in his laboratory.

Professor Siegbahn. Once before, a Swede, to the honour of his country, has won world-wide fame through exact determinations of wavelengths. It was Anders Jonas Angstrom, who investigated the spectrum of light, and whose name survives as the denomination of the unit with which wavelengths are measured in this range of radiation. I now give expression to the pride of the Academy of Sciences in the fact, that once again a Swede, to the honour of his country, has gained a similar world-wide fame, and to her conviction that your work will always be inscribed in the history of the microcosm of the atom. It is a profound joy to us all that you have won this prize, which I now invite you to receive from the hands of His Majesty the King.

MANNE SIEGBAHN

The X-ray spectra and the structure of the atoms

Nobel Lecture, December 11, 1925

We all know that the discovery of X-rays provided the medical sciences with a new and invaluable working tool; and we must all be equally aware that recent developments in the study of X-rays have opened up new paths of investigation in various fields of the natural sciences. One can already point to a whole range of major problems which the use of X-rays has made it possible to solve.

It is obvious that the fact that X-rays are such an important tool for workers in various fields of science forms a very cogent reason for undertaking a thorough investigation of their nature.

It is also clear that, seen from this viewpoint, any investigation of X-radiation must be planned on a broad basis, and cannot be directed solely towards the more or less specialized problems affecting different branches of science.

The study of X-rays is not, however, motivated only by their application in the various sciences such as we have just mentioned. X-rays provide us in addition with an insight into the phenomena within the bounds of the atom. All the information on what goes on in this field of physical phenomena is, so to speak, transmitted in the language of the X-rays; it is a language which we must master if we are to be able to understand and interpret this information properly.

The phrases of the language, in this instance, are made up of electromagnetic waves, and the features of these which we are able to recognize, record, and interpret are in the first place the *wavelength* and *intensity* of this radiation. Experience has taught us that if we concentrate our attention on a particular atom, then a system of waves is emitted from this atom having an entirely fixed composition with respect to the wavelengths involved. These wavelengths are also, in practice, entirely independent of such external circumstances as the chemical or physical forces acting upon the atom concerned. The system of waves is governed solely by the field of force of the atom being studied.

The first task which faces us, if we seek to unlock the mystery of the

atom in this way, will therefore be to find some way of measuring and analysing the wave systems emitted by the atoms of the 92 different elements.

I should like, here, to comment on one point. The problem I have just mentioned might well have been insoluble because of utter complexity in the wave system. We have only to remember how, in the field of ordinary optics, certain spectra are composed of tens of thousands of different wavelengths, and continue to defy all attempts at a preliminary classification. Where the X-radiation from the atom is concerned, however, Nature has been rather more accommodating. Not only are the wave systems peculiar to each type of atom moderately complicated, but also the wave systems belonging to the different atoms show considerable general agreement. This agreement is not, as in normal spectroscopy, confined to the vertical groups of Mendeleev's table, but extends to all elements.

It is noteworthy, therefore, that the general type in which X-ray spectra occur has a far-reaching analogy with precisely the type in the normal spectral range which is to be found in the first vertical group in Mendeleev's table, i.e. the alkali spectra.

In order to be able to demonstrate this, I shall have to say a few words on the subject of obtaining an energy diagram from the observed wave system.

Let us assume that at a given moment a certain atom is in such state that its total energy has the value E_1 . At that moment a rearrangement occurs within the atom which has the effect of reducing the total energy to E_0 . In the course of this process of rearrangement the quantity of energy liberated is therefore :

$$E_1 - E_0$$

We may assume, with Bohr, that this quantity of energy appears in the form of a wave, making up part of the wave system which is characteristic for the atom in question. Its wavelength we may term λ , with a corresponding frequency ν , and we may define ν as the reciprocal value of λ , thus:

$$\nu = \frac{1}{\lambda}$$

According to the Einstein-Bohr formula there is thus a relationship between the frequency ν_1 for the wave and the energy liberated from the atom:

$$\nu_1 = \frac{E_1 - E_0}{h}$$

where h is a universal constant (Planck's constant).

We can therefore imagine that the energy of the atom during a rearrangement of this nature, is then changed from E_2 to E_0 , during which a wave of frequency ν_2 is emitted. Thereby is

$$\nu_2 = \frac{E_2 - E_0}{h}$$

The series can be continued further:

$$\nu_3 = \frac{E_3 - E_0}{h}, \text{ and so on.}$$

By measuring the wavelengths it is possible experimentally to determine a series of ν -values: $\nu_1, \nu_2, \nu_3, \dots$. It would, however, require a special and not always simple analysis of the wavelengths available in order to select and bring together those frequency values which belong to one and the same series. The first person to succeed, within the field of normal spectroscopy,

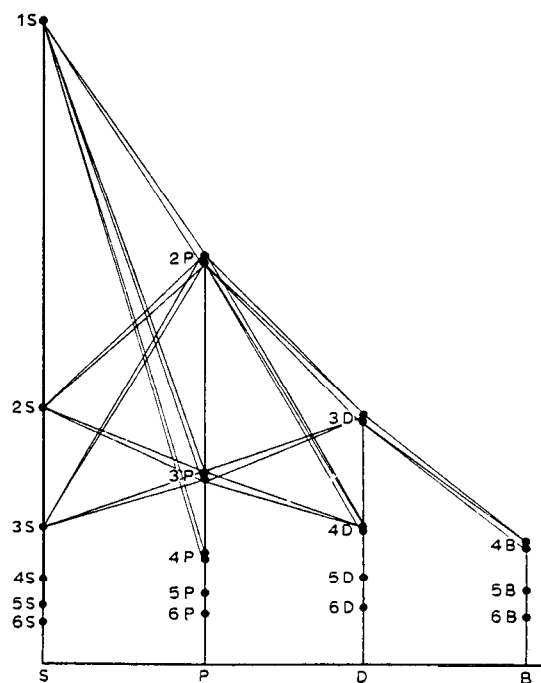


Fig. 1.

in solving this difficult, but for future research fundamental, problem was the Swedish scientist J. R. Rydberg.

Rydberg, namely, found a general formula for the relationship between ν -values forming part of the same series, and he made use of this formula to collect the different series for each separate element from the range of wavelengths available.

For the alkali spectra, in particular, Rydberg found three different series, which he termed the principal series, the sharp, and the diffuse secondary series. These three series have since been supplemented, through new measurements, by a further series commonly known as the Bergman series.

If we now apply the Einstein-Bohr formula we can, by using the known ν -values, disentangle four series of energy values determined with high exactitude relative to each other. These four energy-level series are usually graphically represented as shown in Fig. 1. For each point, the height above the horizontal base line is a measure of the amount of energy characteristic of the state in question. These four series, each shown on a vertical line, are usually termed the s-, p-, d-, and b-series. From the energy series we come according to the formula

$$\nu_1 = \frac{E_1 - E_0}{h}$$

back to the frequency series (shown in Fig. 1 by the inclined lines).

What is characteristic for the optical spectra belonging to the first vertical group of Mendeleev's table, i.e. for the alkali spectra, is the fact that of the four energy series, the s-series consists of simple energy levels, while the three remaining series, that is to say the p-, d-, and b-series, are made up of double levels, as will be seen from Fig. 1 which represents the energy and frequency diagram for potassium.

If we now switch from the optical spectra to X-ray spectra, an examination of the combined results of measurements indicates that the X-ray spectra for all elements can be represented by an energy diagram of exactly the same kind as was previously found for the alkali spectra. This diagram is shown in Fig. 2. Apart from the energy levels corresponding to the s-, p-, d-, and b-series (the vertical lines), there are the observed transitions, spectral lines represented by lines linking the two energy levels which correspond to the initial and final state of the atom when the spectral line in question is emitted. It follows from this that the main series in normal optics matches the K-series in the X-ray spectra. The L-series, on the other hand, is put together from the

In passing judgment on this latter question we can now take into account the results of a study recently carried out by lecturer Axel Jonsson at the Uppsala Institute of Physics. Measurements made hitherto have referred to the X-ray spectra of tungsten and platinum, and they show, with one or two very minor exceptions, a very fine agreement with the intensity conditions in the optical alkali spectra. In some respects, otherwise, this result goes further and deeper than what is the case in the optical field, and the measurements can also be used to get a better insight in the mechanism of radiation itself than has been possible up till now.

If we bring together on the one hand the measurements of wavelength and on the other those of intensity, then we have in them both strong support for the justification of the diagram shown.

What then is the further, deeper reason for the X-ray spectra exhibiting such a far-reaching analogy with the alkali spectra in particular? In fact, the answer is not so difficult to give. An alkali atom consists of an internally completed electron structure of the same type as that of the inert atom next to it, but has in addition a loosely bound valency electron. The optical spectrum is emitted when this loosely bound valency electron moves from one quantum orbit to another. For the X-ray spectra, too, we must assume that light emission takes place when an electron, but in this instance one belonging to the inner electron system of the atom, moves from one quantum orbit to another while the state of all the remaining electrons is not altered to any significant extent.

Quite irrespective of whether the energy diagram should be given this or some other form, X-ray spectroscopy measurements provide us with a quantitative and thorough knowledge of the energy content and energy relationships within each particular atom. Any further work on the structure of the atom must rest upon this firm, empirical foundation.

An energy diagram as complete as that shown in Fig. 2 is, however, only found for the heaviest elements. If we go further down the Mendeleev table towards the lighter elements, one level after the other will stepwise disappear until, when we reach helium and hydrogen, there is only a single energy level. This successive disappearance of the levels is seen in Fig. 3, which shows the diagrams for the inert gases. At the same time the figure shows how the number of X-ray spectrum lines successively decreases, so that for argon, for example, we only find four L-lines apart from the K-series, while there are only two K-lines for neon.

This way of representing the energy diagram for various elements also

gives us a good guidance when we have to extrapolate data from the field of X-ray spectroscopy to that of normal optical spectroscopy. It is then clear that only those spectrum systems in the optical field which allow a representation in the form of an alkali diagram can be considered as a continuation of X-ray spectra. The interpretations of line systems in the optical field as a continuation of known X-ray series which are proposed in some cases is contrary to this first, logical requirement.

Otherwise, the comparison of the diagrams indicates that the chances of rediscovering the actual X-ray series in the optical field are greatest for the heaviest elements, where a large number of levels with small differences in energy occur.

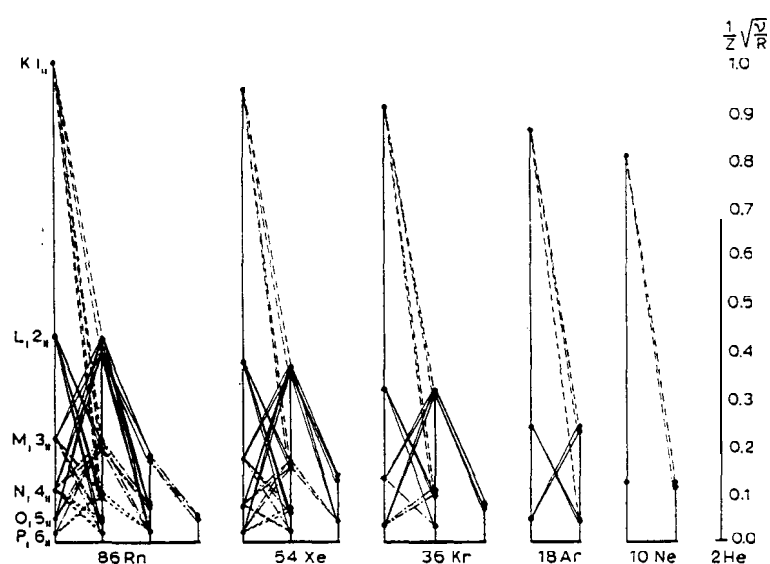


Fig. 3.

We may now ask ourselves whether this diagram of levels is merely a convenient and clear way of representing the results of observations, or whether the diagram, in this or some similar form, has a deeper significance. Thanks to the fact that we can in many cases determine with considerable accuracy the absolute energy value for a number of levels in the diagram, we are, by means of measurements of wavelength in the line spectrum, in a position to state the absolute energy values for all the levels. This diagram, which has now been given for the majority of the elements, thus supplies fundamental information on the energy state of the atom of each element. These are

primary natural constants which are obtained in this manner with the help of X-ray spectroscopy. If we cast our minds back to the work that has, over the years, been devoted to other atomic constants, such as the determination of the atomic weight of the elements, and if we further consider that the atomic weight of most elements is no more than an average value from discontinuously varying group values, and that this is not true of the energy diagram of the elements, then I dare to feel that the efforts which have been directed to finding this energy diagram for the atoms has been fully justified.

This has also, I should like to say, closed the first chapter in the history of X-ray spectroscopy. This work has, however, given rise to new problems which have now to be tackled. Recently, in a lecture to the Swedish Society of Chemists, I drew attention to preliminary studies which are being made in one of these new fields - the matter of the chemical properties of the atoms having an effect upon the phenomenon of X-radiation.

I would like to close this lecture with a short report on a few recent results in another field of study which stems from the X-ray spectroscopy measurement we have been discussing. The very first accurate measurements of X-ray wavelengths using the new precision methods showed us that the accepted law of Bragg was not entirely exact. These experiments, originally carried out by Dr. W. Stenström, were interpreted by him as indicating that X-rays were diffracted when they passed through the surface of the crystal being used as a grating. With the further increases in the accuracy of measurement which have been attained since then, it has become possible employing this method to make extremely accurate quantitative measurements of the refraction of the X-rays in various crystals. The method has also been used in a modified form by a number of American workers. In a letter to the British journal *Nature* about a year ago, E. Hjalmar and I reported on a number of results which seemed to indicate that the refraction in a crystal underwent a discontinuous change when the frequency of the radiation passed the characteristic frequency of the type of atoms making up the crystal. That is to say, we suggested that the experiment must be considered as depending upon an anomalous dispersion.

The analogous phenomenon which has long been known in ordinary optics, where it has been the subject of careful study, has proved to be of fundamental importance for an understanding of the mechanism of radiation itself. It therefore seems to me to be of particular interest to try to find, in the field of X-radiation, some more direct method of obtaining this effect, and perhaps of making quantitative measurements. To this end civil engineer A.

Larsson at the Uppsala Institute of Physics has been making a number of experimental studies using the following method which will give a direct indication of any anomalous dispersion.

A suitably chosen line spectrum is recorded photographically, once with a copper-sulphate crystal and again with a calcium-sulphate crystal. If the spectrum selected is such that it contains spectrum lines on either side of the characteristic radiation frequency of the copper, any anomalous dispersion would betray itself as an irregular shift of the spectrum lines on the plate made with the copper-sulphate crystal compared to the position of the lines on exposure with the other crystal. The results of the exact measurements on the two plates have shown that such is the case. I should add, in conclusion, that the experiment was so arranged as completely to eliminate the differing absorption of radiation on either side of the characteristic frequency of copper.

The demonstration of anomalous dispersion in X-radiation has opened up a new path for further work, a path which seems likely to lead us to new data on one of the most urgent problems of atomic physics today - that of the distribution of electrons within the atom. Only continued experimental work can show how close this path will bring us to our goal.

Biography

Karl Manne Georg Siegbahn was born on the 3rd of December, 1886, at Örebro in Sweden. His father was Nils Reinhold Georg Siegbahn, a station-master of the State Railways, and his mother was Emma Sofia Mathilda Zetterberg.

After receiving a high-school education he entered the University of Lund in 1906, where he obtained his doctor's degree, in 1911, on the thesis «Magnetische Feldmessung». From 1907 to 1911 he served as Assistant to Professor J. R. Rydberg in the Physics Institute of the University, afterwards he was appointed lecturer and (in 1915) Deputy Professor of Physics. On the death of Rydberg, he was appointed Professor (1920). In 1923 he became Professor of Physics at the University of Uppsala. In 1937 came his appointment as Research Professor of Experimental Physics, at the Royal Swedish Academy of Sciences. When the Physics Department of the Nobel Institute of the Academy came into being, that same year, Siegbahn was made its first Director.

Siegbahn's early work (1908-1912) was concerned with problems of electricity and magnetism.

From 1912 to 1937 his research work was mainly devoted to X-ray spectroscopy. He developed new methods, and designed instruments for this purpose. His improvements and new constructions of air pumps and X-ray tubes enabled a considerable increase of the radiation intensity, and the numerous spectrographs and crystal or linear gratings which he constructed, have resulted in a highly increased accuracy of his measurements. In this way, a large number of new series within the characteristic X-radiations of elements could be discovered. The new precision technique thus developed by Siegbahn led to a practically complete knowledge of the energy and radiation conditions in the electron shells of the atoms, while at the same time a solid empirical foundation was created for the quantum-theoretical interpretation of attendant phenomena. Siegbahn's findings in this field have been summarized by him in his book *Spektroskopie der Röntgenstrahlen*, 1923 (rev. ed., 1911; ed. in English, 1924), a classic in scientific literature. As a

measure of the high precision achieved by Siegbahn's spectrographs (which are held at a constant temperature and read, in tenths of seconds, by means of two microscopes mounted diametrically opposite one another on a precision goniometer) may be mentioned the fact that his energy-level values, arrived at thirty years ago, still serve for many purposes.

The research activity in the Institute under Siegbahn's leadership was directed towards problems of nuclear physics. For this purpose a cyclotron was constructed capable of accelerating deuterons of up to 5 to 6 MeV (1939), which was soon to make place for a larger one for deuteron energies of up to 30 MeV. In addition to this, a high-tension generator for 400,000 volts was built, as a provisional measure, during the War (transformed into a plant for 1.5 million volts in 1962). For the purpose of studying the energy and radiation of the different radioactive isotopes an electromagnetic separator has been constructed at the Institute, and several new types of β -spectrographs for various purposes have been designed and built. With these technical resources, and after suitable methods had been developed, a number of important projects for research were taken up. The radiation processes of unstable atomic nuclei and nuclear reactions of various kinds have been studied and exact measurements made of the magnetic properties of atomic nuclei. Other projects tackled by Siegbahn and his staff include the construction of an electron microscope of a new pattern and an automatically working ruling-engine for scratching well-defined gratings (with up to 1,800 lines per mm), especially for X-rays and the extreme ultraviolet field. A large number of young scientists, including many from foreign countries, have taken part in the progressively developed research work to study the atomic nucleus and its radioactive properties.

Siegbahn travelled a great deal and visited practically all important centres of scientific activity in Europe (1908-1922), Canada and the United States (1924-1925), where he, on invitation of the Rockefeller Foundation, gave lectures at the Universities of Columbia, Yale, Harvard, Cornell, Chicago, Berkeley, Pasadena, Montreal, and several other universities. After World War II, he visited the main nuclear research institutes in the U.S.A. during the years 1946 and 1953 (Berkeley, Pasadena, Los Angeles, St. Louis, Chicago, M.I.T. Boston, Brookhaven, Columbia, etc.).

As member of the Commission Internationale des Poids et Mesures (1937) he took part in annual meetings of this Commission in Paris; he was elected honorary member of this Commission when he left his membership (1956). Siegbahn was President of the International Union of Physics, during the

period 1938-1947. Other honours, in addition to the Nobel Prize in Physics (1924) awarded to Professor Siegbahn included the Hughes Medal (1934) and the Rumford Medal (1940) from the Royal Society, London; the Duddel Medal from the Physical Society, London (1948). He is honorary doctor in Freiburg (1931), Bukarest (1942), Oslo (1946), Paris (1952) and the Technical Faculty in Stockholm (1957). He is Member of the Royal Society, London and Edinburgh, of the Académie des Sciences, Paris, and of several other academies.

Professor Siegbahn married Karin Hogborn in 1914. They have two sons : Bo (b. 1915), at present (1964) Ambassador at Morocco; and Kai (b. 1918), since 1954 Professor of Physics at the University of Uppsala, on the same Chair that his father held during 1923-1937.

Physics 1925

JAMES FRANCK

GUSTAV HERTZ

«*for* their discovery of the laws governing the impact of an electron
upon an atom »

Physics 1925

*Presentation Speech by Professor C. W. Oseen, member of the Nobel Committee
for Physics of the Royal Swedish Academy of Sciences*

Your Majesty, Your Royal Highnesses, Ladies and Gentlemen.

The Physics Nobel Prize for the year 1925 has been awarded to Professor James Franck and Professor Gustav Hertz for their discovery of the laws governing the impact of an electron upon an atom.

The newest and most flourishing branch of the great tree of physical research is atomic physics. When Niels Bohr founded this new science in 1913, the material at his disposal consisted of data concerning the radiation of glowing bodies, which had been accumulated over several decades. One of the earliest findings in the field of spectroscopy was that the light emitted by a glowing gas when observed through a spectroscope, splits up into a large number of different lines, called spectral lines. The fact that simple relationships exist between the wavelengths of these spectral lines, was first discovered by Balmer in 1885 for the hydrogen spectrum, and demonstrated later by Rydberg for a large number of elements. Two questions relating to theoretical physics arose as a result of these discoveries: How is it possible for a single element to produce a large number of different spectral lines? And what is the fundamental reason behind the relationships that exist between the wavelengths of the spectral lines of a single element? A large number of attempts were made to answer these two questions, on the basis of the physics which we are now accustomed to call classical physics. All were in vain. It was only through a radical break with classical physics that Bohr was able to resolve the spectroscopic puzzles in 1913. Bohr's basic hypotheses can be formulated as follows:

Each atom can exist in an unlimited number of different states, the so-called stationary states. Each of these stationary states is characterized by a given energy level. The difference between two such energy levels, divided by Planck's constant h , is the oscillation frequency of a spectral line that can be emitted by the atom. In addition to these basic hypotheses, Bohr also put forward a number of specific hypotheses, with the aid of which it was possible to calculate the spectral lines of the hydrogen atom and the helium ion. The extraordinarily good agreement with experience obtained in this way,

-explains why after 1913 almost a whole generation of theoretical and experimental physicists devoted itself to atomic physics and its application in spectroscopy.

Bohr's more specific assumptions have had the same fate as that which sooner or later overtakes most physical hypotheses: science outgrew them. They have become too narrow in relation to all the facts which we now know. For a year now attempts have been made to solve the puzzle of the atom in other ways. But the new theory which is now in process of being established, is yet not a completely new theory. On the contrary, it can be termed a further development of Bohr's theory, because among other things in it Bohr's basic assumptions remain completely unchanged. In this overthrowing of old ideas, when all that has been gamed in the field of atomic Physics seemed to be at stake, there is nobody who would have thought it advisable to proceed from the assumption that the atom can exist in different states, each of which is characterized by a given energy level, and that these energy levels govern the spectral lines emitted by the atoms in the way described. The fact that Bohr's hypotheses of 1913 have succeeded in establishing this, is because they are no longer mere hypotheses but experimentally proved facts. The methods of verifying these hypotheses are the work of James Franck and Gustav Hertz, for which they have been awarded the Physics Nobel Prize for 1925.

Franck and Hertz have opened up a new chapter in physics, viz., the theory of collisions of electrons on the one hand, and of atoms, ions, molecules or groups of molecules on the other. This should not be interpreted as meaning that Franck and Hertz were the first to ask what happens when an electron collides with an atom or a molecule, or that they were the originators of the general method which paved the way for their discoveries and which consists of the study of the passage of a stream of electrons through a gas. The pioneer in this field is Lenard. But Franck and Hertz have developed and refined Lenard's method so that it has become a tool for studying the structure of atoms, ions, molecules and groups of molecules. By means of this method and not least through the work of Franck and Hertz themselves, a great deal of material has been obtained concerning collisions between electrons and matter of different types. Although this material is important, even more important at the present time is the general finding that Bohr's hypotheses concerning the different states of the atom and the connexion between these states and radiation, have been shown to agree completely with reality.

Professor Franck. Professor Hertz. Through clear thinking and painstaking experimental work in a field which is continuously being flooded by different hypotheses, you have provided a firm footing for future research. In gratitude for your work and with sincere good wishes I request you to receive the Physics Nobel Prize for 1925 from the hands of our King.

JAMES FRANCK

Transformations of kinetic energy of free electrons into excitation energy of atoms by impacts

Nobel Lecture, *December 11*, 1926

Ladies and gentlemen!

The exceptional distinction conferred upon our work on electron impacts by the Royal Swedish Academy of Sciences requires that my friend Hertz and I have the honour of reporting to you on current problems within this province :

The division of the material between us left me with the task of presenting, in a historical setting, the development of these projects which have led to an association with Bohr's atomic theory.

Investigations of collision processes between electrons, atoms and molecules have already got well under way. Practically all investigations into the discharge of electricity through gases can be considered under this heading. An enormous amount of knowledge, decisive for the whole development of modern physics, has been gained, but it is just in this gathering that I feel it is unnecessary for me to make any special comment, since the lists of the men whom the Swedish Academy of Sciences have deemed worthy of the Nobel Prize contain a large number of names of research workers who have made their most significant discoveries in these fields.

Attracted by the complex problems of gas discharges and inspired particularly by the investigations of my distinguished teacher E. Warburg, our interest turned in this direction. A starting-point was provided by the observation that in inert gases (and as found later, also in metal vapour) no negative ions were formed by the attachment of free electrons to an atom. The electrons remained rather as free ones, even if they were moving slowly in a dense gas of this type, which can be inferred from their mobility in an electric field. Even the slightest pollution with normal gases produced, at once, a material attachment of the electrons and thus the appearance of normal negative ions.

As a result, one can perhaps divide gases somewhat more clearly than has been the case up to now from the observations described in the literature, into one class with, and one class without, an electron affinity. It was to be

expected that the motion of electrons in gases of the latter kind would obey laws of a particularly simple kind. These gases have exhibited special behaviour during investigations of other kinds into gas discharges. For instance, according to Ramsay and Collie, they have a specially low dielectric strength, and this was, further, extremely dependent upon the degree of purity of the gas (see, for example, Warburg's experiments). The important theory of the dielectric strength of gases, founded by Townsend, the equations of which even today, when used formally, still form the basic foundation of this field failed in these cases. The reason for this seemed likely to be that Townsend's hypothesis on the kind of collisions between slow electrons and atoms, particularly inert-gas atoms, differed from the reality, and it seemed promising to arrive at a kinetic theory of electrons in gases by a systematic examination of the elementary processes occurring when collisions took place between slow electrons and atoms and molecules. We had the experiences and techniques to support us, which men like J. J. Thomson, Stark, Townsend, and in particular, however, Lenard, had created, and also had their concept of the free path-lengths of electrons and the ionization energy, etc., to make use of.

The free path-lengths in the light inert gases were examined first. By <<freepath>> in this connection is to be understood that path which, on the average, is that which an electron traces between two collisions with atoms along a straight track. The distance is measurable as soon as the number of atoms per unit volume is sufficiently small, this being attained by taking a low gas pressure. The method of measurement itself differed but slightly from that developed by Lenard. It is unnecessary to go into closer detail since the results gave the same order of values for the free path-length as Lenard obtained for slow electrons in other gases. The value is of that order which is obtained by calculation if the formulas of the kinetic gas theory are used for the free path-length, taking for the impact radius of the electron a value which is very small compared with the gas-kinetic atom radii. With this assumption, the electrons behave, to a first approximation, like a gaseous impurity in the inert gas, not reacting chemically with it – an impurity, however, which has the special quality of consisting of electrically charged particles and having a vanishingly small impact radius. As a result of significant experiences, we know, today, from the work of Ramsauer and others on the free path-lengths of electrons in heavy inert gases that the picture we had formed at that time was a very rough one, and that for collisions of slow electrons the laws of quantum theory are of far more significance than the

mechanical diameter, but as a first approximation for the establishment of the kinetics it suffices. Further, it also sufficed, as it turned out, to gain an understanding of the energy conversion on the occurrence of a collision between the slow electrons and the atoms of the inert gases and metal vapours. Since the mass of the electron is 1800 times smaller than that of the lightest atom we know, the hydrogen atom, the transfer of momentum from the light electron to the heavy atom during customary gas-kinetic collisions, i.e. collisions such as between two elastic balls, must be exceptionally small according to the laws of momentum. A slow electron with a given amount of kinetic energy, meeting an atom at rest, ought to be reflected without practically any energy loss, much the same as a rubber ball against a heavy wall. These elastic collisions can now be pursued by measurements.

I will pass over the detection of the single reflection and mention in more detail a simple experimental arrangement which, by means of an accumulation of collisions, enables us to measure the energy loss which is otherwise too small to measure in one elementary process. The mode of action might well be clear from a schematic layout (Fig. 1).

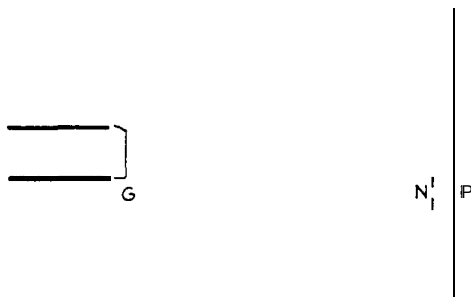


Fig. 1.

G indicates the electron source. It consists of a tungsten wire, heated to a bright-red glow by an electric current. That such a glowing wire is a source of electrons can, I think, be taken as read in this age of radio. A few centimetres away is a wire-screen electrode N. If we now charge the screen positively with respect to the glowing wire, by means of an accumulator, the electrons emitted by the wire towards the screen will be accelerated. The kinetic energy which the electrons must gain through this acceleration can easily be found for the case where no gas exists between G and N, that is, when the electrons fall through the field of force freely without collisions. We have the relationship :

$$\frac{1}{2}mv^2 = e \cdot V$$

Here, $\frac{1}{2}mv^2$ is the kinetic energy of each electron, e is its electrical elementary charge, and V the applied potential difference. If the latter is measured in volts, then, for instance, the kinetic energy of an electron which has fallen through 10 volts is approximately 10^{-11} ergs. We have become accustomed to speak of x -volt electrons, and to simply denote the acceleration voltage (x volts) as a measure of energy. Thus in our arrangement the electrons fall upon the screen with an energy of x volts (the potential difference between G and N). Some of the electrons are caught by the screen, some fly through the mesh. The latter, assuming no field between N and P which would throw the electrons back, all reach the electrode P and produce a negative current which flows to earth through a galvanometer. By introducing an electric field between N and P the energy distribution of those electrons passing through the screen can be determined. If, for example, we take only 4-volt beams, which pass perpendicularly through the screen, then the electron current measured at the galvanometer as a function of a decelerating potential difference applied between N and P , must be constant, until P becomes 4 volts more negative than N . At this point the current must become suddenly zero since henceforth all electrons will be so repelled from P that they return to N . If now we introduce an inert gas such as helium or a metal vapour between the three electrodes and choose such a pressure as will ensure that the electrons between G and N will make many impacts upon atoms, whilst passing freely through the space between N and P , we can determine, by plotting the energy distribution of the electrons arriving at P , whether the electrons have lost energy by impacts on the atoms. In discussing the resulting current-voltage curve it should be noted that the electrons no longer pass through the screen mesh perpendicularly, but are scattered in all directions due to reflection from the atoms. As a result of this, there is an easily calculable change in shape of the curve, and this holds, too, for uniform kinetic energy of the electrons. From a consideration of the resulting curves it was found that for not too high pressures, particularly for monatomic gases of high atomic weight, the kinetic energy of slow electrons was the same as for those in vacuum under the same acceleration voltage. The gas complicates the trajectory of the electrons in the same way that a ball's trajectory is affected by rolling down a sloping board bedecked with a large number of nails, but the energy (because of the large mass of the atom compared with that of the electron) is practically the same as for conditions of free fall. Only for high pressures, that is, with the occurrence of many thousands of collisions, can the energy loss corresponding to elastic

collision be demonstrated.* A calculation of the number of collisions was later carried out by Hertz. Taking this as a basis and evaluating the curves measured for higher pressures accordingly, it emerges that, for example, energy is transferred to a helium atom amounting to $1.2-3.0 \times 10^{-4}$ of the energy of the electron prior to the collision, whilst the calculated value for the mass ratio under conditions of pure mechanical elastic impact is 2.9×10^{-4} . We may therefore, with close approximation to reality, speak of elastic collisions.

For polyatomic gases a significantly greater average energy loss was determined. Using the methods available at that time, it was not possible to distinguish whether this latter effect was contingent upon attachment of the electrons to the molecule, that is, the formation of negative ions, or whether a transfer of the kinetic energy of the striking electrons into vibrational and rotational degrees of freedom of the molecules was taking place. An investigation just carried out in my institute by Mr. Harries shows that the latter elementary process, even though at a low level, does occur, and is important in the explanation of the energy losses.

Can the principles of action found for slow electrons in the case of elastic collisions hold good for higher electron velocities? Apparently not, for the elementary knowledge of gas discharges teaches us that with faster electrons, i.e. with cathode rays, the impacted atoms are excited to luminescence or become ionized. Here, energy of the impacting electrons must be transferred into internal energy of the impacted atoms, the electrons must henceforth collide inelastically and give up greater amounts of energy. The determination of the least amount of energy which an electron must possess in order to ionize an atom was therefore of interest. Measured in volts, this energy is called the ionization voltage. Calculations of this value of energy by Townsend were available for some gases and these were based upon the validity of his assumptions about the course of the elementary action on collision. I mentioned already the reasons for doubting the correctness of these indirectly determined values. A direct method had been given by Lenard, but it gave the same ionization voltage for all gases. Other writers had obtained the same results within the range of measurement. We therefore repeated Lenard's investigations, using the improved pumping techniques which had become available in the meantime, and obtained characteristic, marked differences in values for the various gases. The method used by

* It is better to use here the experimental arrangements indicated later by Compton and Benade, Hertz, and others.

Lenard was as follows. Electrons, from a glowing wire, for example, were accelerated by a suitable electric field and allowed to pass through a screen grid into a space in which they suffered collisions with atoms. By means of a strong screening field these particular electrons were prevented from reaching an electrode to which was connected a measuring instrument. Atoms ionized by the impact resulted in the newly formed positive ions being accelerated through the screening field, which repelled the electrons, towards the negatively charged electrode. A positive current was thus obtained as soon as the energy of the electrons was sufficient for ionization to take place. I will talk later about the fact that a positive charge appears if the impacted atoms are excited to emit ultraviolet light, and that, as shown later, the charges measured at that time are to be attributed to this process and not to ionization, as we formerly supposed.

In any case, as already discussed, inelastic collisions were to be expected between electrons and atoms for the characteristic critical voltages appertaining to each kind of atom. And it proved easy to demonstrate this fact with the same apparatus as was used for the work on elastic collisions. Measurement of the energy distribution of the electrons, on increasing the accelerating voltage above the critical value, showed that electrons endowed with the critical translation energy could give up their entire kinetic energy on collision, and that electrons whose energy exceeded the critical by a fraction, likewise gave up the same significant amount of energy, the rest being retained as kinetic energy. A simple modification of the electric circuit diagram of our apparatus produced a significantly sharper measurement of the critical voltage and a visual proof of the discontinuously occurring release of energy from the electrons on collision. The measurement method consisted of measurements of the number of those electrons (possessing markedly different energies from zero after many collisions) as a function of the accelerating voltage.

The graph (Fig. 2) shows the results of measurements of electron current in mercury vapour. In this case, all electrons whose energy is greater than the energy of $\frac{1}{2}$ volt beams were measured. It can be seen that in Hg vapour this partial electron current increases with increasing acceleration, similar to the characteristic of « glow-electron » current in vacuum, until the critical energy stage is reached when the current falls suddenly to almost zero. Since the electrons cannot lose more or less than the critical amount of energy, the cycle begins anew with further increase of voltage. The number of electrons whose velocity is greater than $\frac{1}{2}$ volt, again climbs up until the critical value is

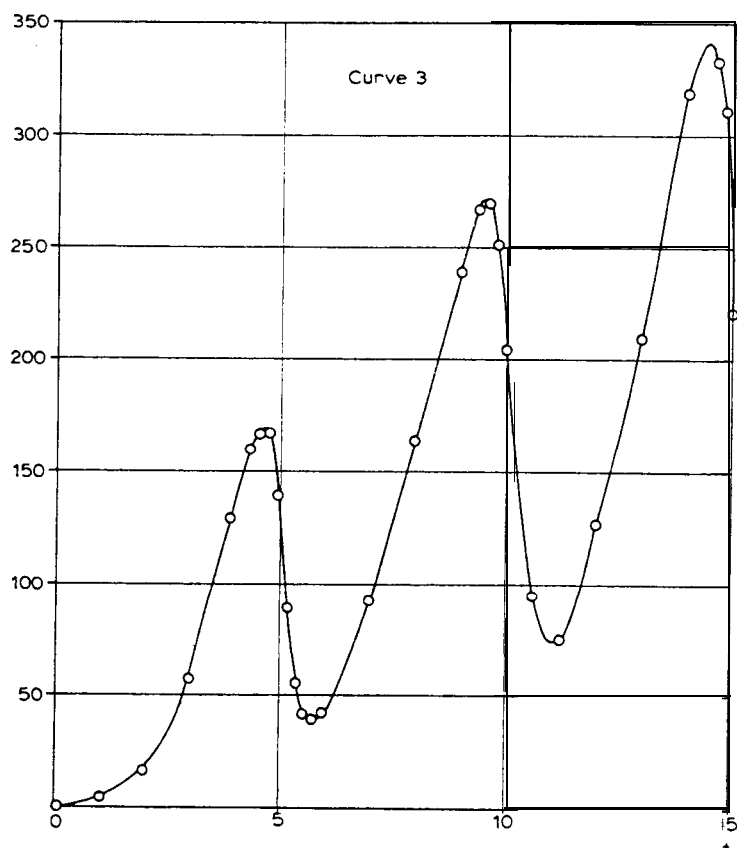


Fig. 2.

reached, the current again falls away. The process repeats itself periodically as soon as the accelerating voltage overreaches a multiple of the critical voltage. The distance between the succeeding maxima gives an exact value of the critical voltage. This is 4.9 V for mercury vapour.

As already mentioned we took this value to be the ionization voltage (the same applied to He which was determined by the same method and was about 20 V). Nevertheless, the quanta-like character of the energy transfer could not help but remind us—who practically from the start could witness from nearby the developments of Planck's quantum theory—to the use of the theory made by Einstein to explain the facts of the photoelectric effect ! Since here, light energy is converted into the kinetic energy of electrons, could not perhaps, in our case, kinetic energy from electrons be converted into light energy? If that were the case, it should be easy to prove in the case of mercury; for the equation $\frac{1}{2}mv^2 = h\nu$ referred to a line of 2,537 Å which is

easily accessible in the ultraviolet region. This line is the longest wavelength absorption line of Hg vapour. It is often cited as Hg-resonance line since R.W. Wood has carried out with it his important experiments on resonance fluorescence. If the conjectured conversion of kinetic energy into light on impact should take place, 'then on bombardment with 4.9 eV electrons, the line 2,537 Å, and only this line out of the complete line spectrum of mercury, should appear.

Fig. 3 shows the result of the experiment. Actually, only the 2,537 Å line appears in the spectrogram next to a continuous spectrum in the long-wave region emitted by the red-glowing filament. (The second spectrogram shows the arc spectrum of mercury for comparison.) The first works of Niels Bohr on his atomic theory appeared half a year before the completion of this work. Let us compare, in a few words, the basic hypothesis of this theory with our results.

According to Bohr an atom can absorb as internal energy only discrete quantities of energy, namely those quantities which transfer the atom from one stationary state to another stationary state. If following on energy supply an excited state results from a transfer to a stationary state of higher energy, then the energy so taken up will be radiated in quanta fashion according to the $h\nu$ relationship. The frequency of the absorption line having the longest wavelength, the resonance line, multiplied by Planck's constant, gives the energy required to reach the first state of excitation. These basic concepts agree in very particular with our results. The elastic collisions at low electron velocities show that for these impacts no energy is taken up as inner energy, and the first critical energy step results in just that amount of energy required for the excitation of the longest wave absorption line of Hg. Subse-

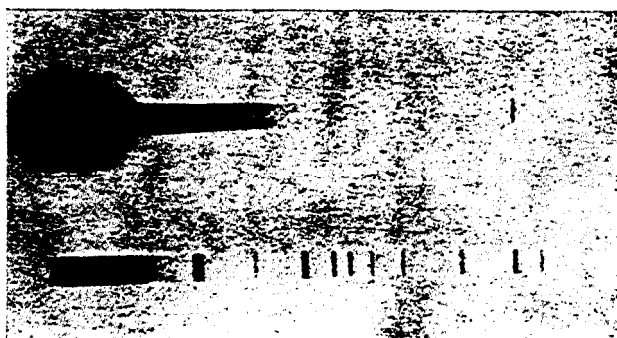


Fig. 3.

quently it appeared to me to be completely incomprehensible that we had failed to recognize the fundamental significance of Bohr's theory, so much so, that we never even mentioned it once in the relevant paper. It was unfortunate that we could not rectify our error (due in part to external circumstances) ourselves by clearing up the still existing uncertainties experimentally. The proof that only monochromatic light was radiated at the first excitation step, as Bohr's theory required, and that the gas is not simultaneously ionized (as we were also obliged to think for reasons other than those mentioned) came about instead during the war period through suggestions from Bohr himself and from van der Bijl. The appearance of positive charge at the first excitation step in Lenard's arrangement was explained by them on the basis of a photoelectric effect at the collector electrode, an hypothesis which was substantiated by Davis and Goucher.

Time does not allow me to describe how our further difficulties were clarified in the sense of Bohr's theory. And in regard to further development, too, I would like to devote only a few words, particularly since my friend Hertz's lecture covers it more closely. The actual ionization voltage of mercury was for the first time determined by Tate as being 10.3 volts, a value which agreed exceptionally well with that resulting, according to Bohr, from the limit of the absorption series. A great number of important, elegantly carried out, determinations of the first excitation level and the ionization voltage of many kinds of atoms was made during the war years and also in the following years, above all by American scientists; research workers such as Foote and Mohler, K. T. Compton and others are to be thanked for extensive clarification in this field.

Without going into details of the experimental arrangements, I should like to mention that it later proved successful, by the choice of suitable experimental conditions, to demonstrate also, from the current-voltage curves, the stepwise excitation of a great number of quantum transitions, lying between the first excitation level and ionization. A curve plotted for mercury vapour might well serve again as an example. It shows the quantum-like appearance of higher excitation levels by kinks in the curve (Fig. 4). It is noteworthy that, in addition, transitions which under the influence of light according to Bohr's correspondence principle do not appear, manifest themselves clearly. When, as is the case with mercury, and still more decidedly so with helium, the first transition is such that it cannot be achieved by light, we have excited atoms in a so-called metastable state. The discovery of a metastable state by means of the electron-impact method was first suc-

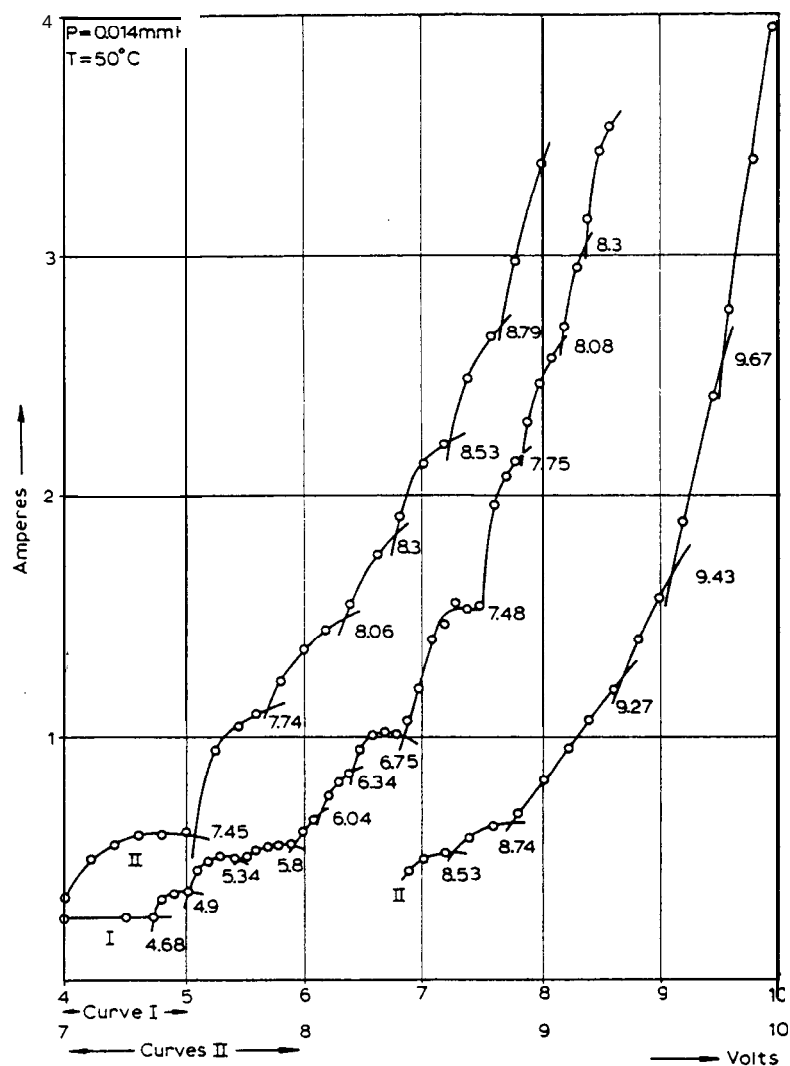


Fig. 4.

cessful with helium. Since helium is a gas in which the absorption series lies in the far ultraviolet-it was later found optically by Lyman-and on the other side, helium, apart from hydrogen, is the most simply constructed atom, the approximate determination of the energy levels of helium and perhaps too, the appearance, in particular, of the metastable level has proved useful for the development of Bohr's theory.

Much more could be said, but I think I have given you the main outline as far as is possible within the framework of a short survey, and must there-

fore draw to a close. The desire to describe, historically, our part in the development of the investigations leading to the establishment of the quantum transfer of energy to the atom by impacting electrons has forced me to take up your time with the description of many a false trail and roundabout path which we took in a field in which the direct path has now been opened by Bohr's theory. Only later, as we came to have confidence in his leadership, did all difficulties disappear. We know only too well that we owe the wide recognition that our work has received to contact with the great concepts and ideas of M. Planck and particularly of N. Bohr.

Biography

James Franck was born on August 26, 1882, in Hamburg, Germany. After attending the Wilhelm Gymnasium there, he studied mainly chemistry for a year at the University of Heidelberg, and then studied physics at the University of Berlin, where his principal tutors were Emil Warburg and Paul Drude. He received his Ph.D. at Berlin in 1906 under Warburg, and after a short period as an assistant in Frankfurt-am-Main, he returned to Berlin to become assistant to Heinrich Rubens. In 1911, he obtained the «*venia legendi*» for physics to lecture at the University of Berlin, and remained there until 1918 (with time out for the war in which he was awarded the Iron Cross, first class) as a member of the physics faculty having achieved the rank of associate professor.

After World War I, he was appointed member and Head of the Physics Division in the Kaiser Wilhelm Institute for Physical Chemistry at Berlin-Dahlem, which was at that time under the chairmanship of Fritz Haber. In 1920, Franck became Professor of Experimental Physics and Director of the Second Institute for Experimental Physics at the University of Göttingen. During the period 1920-1933, when Göttingen became an important center for quantum physics, Franck was closely cooperating with Max Born, who then headed the Institute for Theoretical Physics. It was in Göttingen that Franck revealed himself as a highly gifted tutor, gathering around him and inspiring a circle of students and collaborators (among them: Blackett, Condon, Kopfermann, Kroebel, Maier-Leibnitz, Oppenheimer, and Rabino-vich, to mention some of them), who in later years were to be renowned in their own fields.

After the Nazi regime assumed power in Germany, Franck and his family moved to Baltimore, U.S.A., where he had been invited to lecture as Speyer Professor at Johns Hopkins University. He then went to Copenhagen, Denmark, as a guest professor for a year. In 1935, he returned to the United States as Professor of Physics at Johns Hopkins University, leaving there in 1938 to accept a professorship in physical chemistry at the University of Chicago. During World War II Franck served as Director of the Chemistry

Division of The Metallurgical Laboratory at the University of Chicago, which was the center of the Manhattan District's Project.

In 1947, at the age of 65, Franck was named professor emeritus at the University of Chicago, but he continued to work at the University as Head of the Photosynthesis Research Group until 1956.

While in Berlin Professor Franck's main field of investigation was the kinetics of electrons, atoms, and molecules. His initial researches dealt with the conduction of electricity through gases (the mobility of ions in gases). Later, together with Hertz, he investigated the behaviour of free electrons in various gases-in particular the inelastic impacts of electrons upon atoms-work which ultimately led to the experimental proof of some of the basic concepts of Bohr's atomic theory, and for which they were awarded the Nobel Prize, for 1925. Franck's other investigations, many of which were carried out with collaborators and students, were also dedicated to problems of atomic physics - those on the exchange of energy of excited atoms (impacts of the second type, photochemical researches), and optical problems connected with elementary processes during chemical reactions.

During his period at Göttingen most of his studies were dedicated to the fluorescence of gases and vapours. In 1925, he proposed a mechanism to explain his observations of the photochemical dissociation of iodine molecules. Electronic transitions from a normal to a higher vibrational state occur so rapidly, he suggested, that the position and momenta of the nuclei undergo no appreciable change in the process. This proposed mechanism was later expanded by E. U. Condon to a theory permitting the prediction of most-favoured vibrational transitions in a band system, and the concept has since been known as the Franck-Condon principle.

Mention should be made of Professor Franck's courage in following what was morally right. He was one of the first who openly demonstrated against the issue of racial laws in Germany, and he resigned from the University of Göttingen in 1933 as a personal protest against the Nazi regime under Adolf Hitler. Later, in his second homeland, his moral courage was again evident when in 1945 (two months before Hiroshima) he joined with a group of atomic scientists in preparing the so-called « Franck Report » to the War Department, urging an open demonstration of the atomic bomb in some uninhabited locality as an alternative to the military decision to use the weapon without warning in the war against Japan. This report, although failing to attain its main objective, still stands as a monument to the rejection by scientists of the use of science in works of destruction.

In addition to the Nobel Prize, Professor Franck received the 1951 Max Planck Medal of the German Physical Society, and he was honoured, in 1953, by the university town of Göttingen, which named him an honorary citizen. In 1955, he received the Rumford Medal of the American Academy of Arts and Sciences for his work on photosynthesis, a subject with which he had become increasingly preoccupied during his years in the United States. In 1964, Professor Franck was elected as a Foreign Member of the Royal Society, London, for his contribution to the understanding of exchanges of energy in electron collisions, to the interpretation of molecular spectra, and to problems of photosynthesis.

Franck was first married (1911) to Ingrid Josefson, of Göteborg, Sweden, and had two daughters, Dagmar and Lisa. Some years after the death of his first wife, he was married (1946) to Hertha Sponer, Professor of Physics at Duke University in Durham, North Carolina (U.S.A.).

Professor Franck died in Germany on May 21, 1964, while visiting in Göttingen.

G U S T A V H E R T Z

The results of the electron-impact tests in the light of Bohr's theory of atoms

Nobel Lecture, December 11, 1926

The significance of investigations on the ionization of atoms by electron impact is due to the fact that they have provided a direct experimental proof of the basic assumptions of Bohr's theory of atoms. This lecture will summarize the most important results, and show that they agree in every detail, so far as can be observed at present, with what we should expect on the basis of Bohr's theory.

The fact that atoms are capable of exchanging energy with electromagnetic radiation, led the classical physicists to conclude that atoms must contain moving electrical charges. The oscillations of these charges produce the emission of light radiation, while light absorption was ascribed to forced oscillations of these charges owing to the electrical field of the light waves. On the basis of Lorentz's theory of the normal Zeeman effect, of the magnetic splitting of the spectral lines, it was concluded that these moving charges must be the electrons to which we are acquainted in cathode rays. If only one or several spectral lines were associated with each type of atom, then it might be assumed that the atom contained, for each spectral line, an electron of corresponding characteristic frequency. In reality, however, the number of spectral lines emitted by each atom is infinitely large. The spectral lines are certainly not randomly distributed, on the contrary there exists a certain relationship between their frequencies, but this relationship is such that it is impossible on the basis of classical physics to explain it in terms of the characteristic frequencies of a system of electrons. Here Bohr stepped in with his atomic theory. He applied Planck's quantum theory to the problem of atomic structure and light emission, and thereby greatly extended this theory. It is well-known that Planck, in evolving the law of heat radiation was in contradiction to classical physics. He had come to the conclusion that the processes of emission and absorption of light did not obey the laws of classical mechanics and electrodynamics. In Planck's quantum theory it is assumed that emission and absorption of monochromatic radiation can occur only in an electrical oscillator of the same frequency, moreover that in such proces-

ses the energy must be emitted or absorbed in discrete quantities only. According to Planck, the magnitude of such a quantum is proportional to the frequency of the radiation. The proportionality factor is Planck's constant $h = 6.55 \times 10^{-27}$ erg sec, which is fundamental to the entire later development. Bohr realized that the simple picture of emission and absorption by an oscillating electron and hence the connection between the frequency of the light wave and that of the oscillating electron, was inadequate in explaining the laws governing line spectra. But he retained from Planck's theory the basic relationship between the radiation frequency and the magnitude of the emitted and absorbed energy quanta, and based his atomic theory on the following fundamental assumptions :

- (1) For every atom there is an infinite number of discrete stationary states, which are characterized by given internal energy levels in which the atom can exist without emitting radiation.
- (2) Emission and absorption of radiation are always connected with a transition of the atom from one stationary state to another, emission involving transition to a state of lower energy, and absorption involving transition to a state of higher energy.
- (3) The frequency of the radiation emitted or absorbed respectively during such a transition is given by the equation

$$h\nu = E_1 - E_2$$

where h is Planck's constant and E_1 and E_2 denote the energy of the atom in the two stationary states.

These basic assumptions were supplemented by special theories concerning the nature of the motion of the electrons in the atom, and here Bohr adopted Rutherford's theory that the atom consists of a positive nucleus and of a number of electrons, the total charge of the electrons being equal to the charge of the nucleus. By means of equations also containing Planck's constant, the possible states of motion are determined. These can be considered to be stationary states of the atom. The laws of the motion of the electrons in the atom constituted a major part of Bohr's theory, and in particular have enabled us to calculate the Rydberg constant on the basis of thermal and electrical data, and explain the Periodic System of the elements; however, we need not deal with them in detail here. One fact only is of importance with regard to the electron-impact tests, namely that the set of stationary states of an atom associated with a series spectrum, corresponds to a gradual decrease in binding energy of one of the electrons of atom. Moreover, the

successive stationary states differ by progressively smaller amounts of binding energy of the electron, and converge towards the state of total separation of the electron from the atom.

As an example of series spectra we will now take the simplest case, the spectrum of the hydrogen atom. The frequencies of all the lines in this spectrum can be obtained with great accuracy from the formula

$$\nu = R \left(\frac{1}{m^2} - \frac{1}{n^2} \right)$$

where m and n can represent any integers. Every line is associated with a given value of m , while n ranges over the series of integers from $m+1$ to ∞ . In this way the lines form series; thus, for example, for $m = 2$ we get the well-known Balmer series which is shown diagrammatically in Fig. 1. The characteristic arrangement of the lines, with an accumulation of lines when approaching a given limiting frequency, the so-called series limit, is found in all spectral line series.

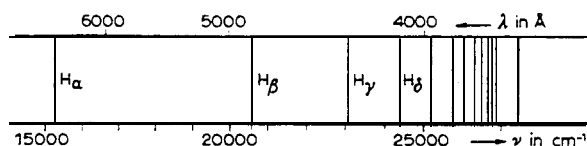


Fig. 1.

In the above formula the frequency of a given spectral line is equated to the difference between two quantities, each of which can assume an infinite series of discrete values. The interpretation of these quantities in the sense of Bohr's theory follows directly from the basic assumptions of this theory: apart from a numerical factor, they are equal to the energy of the atom in its various stationary states. Closer consideration shows that here the energy has to be given a minus sign, i.e. a lower energy is associated with a smaller value of m or n . Thus, the lines of a series correspond to transitions from a series of initial states of higher energy to one final state.

Fig. 2 illustrates diagrammatically the origination of the series associated with the first four stationary states of the hydrogen atom.

In the other elements the situation is in varying degrees more complicated than in the case of hydrogen. All series spectra however have one property in common with that of hydrogen; this is the property represented by the Ritz combination principle, which states that the frequencies of the individu-

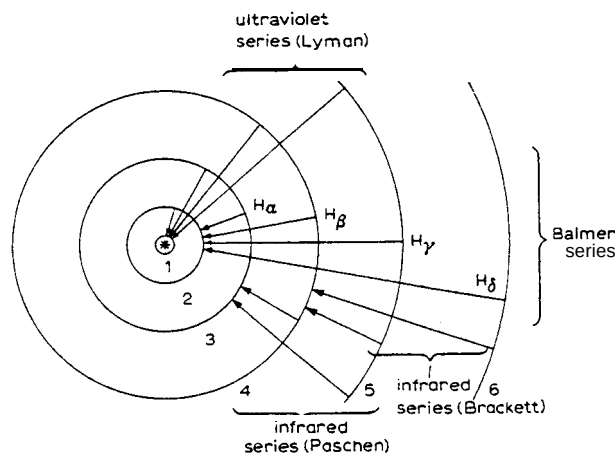


Fig. 2.

al spectral lines are always represented as differences between one or more series of discrete numerical values. These numerical values, the so-called terms, replace the quantities R/n^2 in the case of hydrogen. They differ from these quantities since the formulae representing their values are more complicated, but they agree with these quantities in so far as the differences between the successive terms become smaller and smaller and the term values converge towards zero as the current number n increases.

As an example, Fig. 3 represents diagrammatically the spectrum of mercury. The individual terms are shown by short horizontal lines with the current number at the side of them, and they are arranged in increasing order with the highest term at the top, so that the value of a term can be determined from its distance from the straight line running across the top of the figure. The terms are also presented in the figure in such a way that for a given series they always appear in a column, so that it can be seen how the terms of such a series come closer and closer together as the current number increases, finally converging towards zero. We need not discuss here the reasons for this particular arrangement of the terms. What is important, is that the frequency of every spectral line is equal to the difference between two terms. Thus, a certain combination of two terms is associated with each line. In Fig. 3 some of the lines of the mercury spectrum are indicated by a straight line connecting the two terms with which the line in question is associated. It should be noted that the length of these straight connecting lines is of no physical importance, the frequency of the line depends solely on the difference between the two terms, i.e. the difference between their heights in

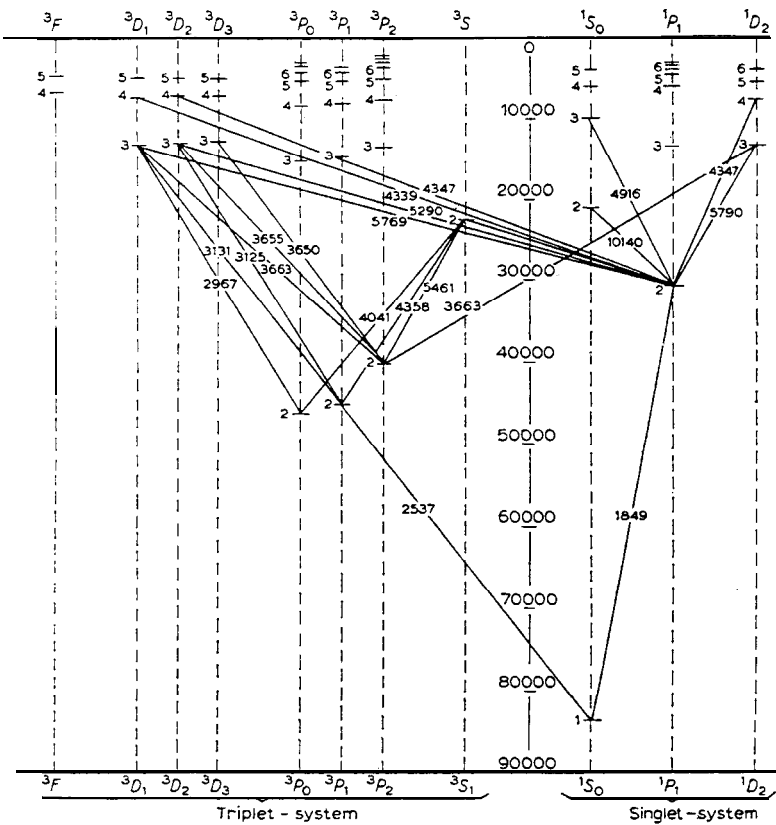


Fig. 3.

Fig. 3. Incidentally, the scale included in Fig. 3 gives the terms not in frequencies but in the unit of wave numbers (reciprocal of the wavelength) commonly used in spectroscopy.

In exactly the same way as in the above case of hydrogen, we now come to the interpretation of this diagram by the Bohr theory.

A comparison of the relation between the frequency of a spectral line and the corresponding two terms namely :

$$\nu = T_1 - T_2$$

on the one hand and the Bohr frequency condition namely:

$$h\nu = E_1 - E_2$$

on the other hand, leads to the following equation:

$$T_n = -\frac{E_n}{h}$$

Thus, according to Bohr, the spectral terms denote the energy levels of the atom in the various stationary states, divided by Planck's constant and prefixed by a minus sign. The reason why the energy levels are negative here, is simply due to the omission of an arbitrary constant which has always to be added to the energy; here it is omitted because we are simply determining the energy differences. Since in our Fig. 3 the terms are arranged in vertical columns with the highest term at the top, the corresponding energy levels rise from the bottom to the top; hence the term diagram gives a direct indication of the energy levels at which the atom can exist in its stationary states. The minimum level energy is associated with the stationary state of the atom from which further transitions to states of still lower energy are impossible. The term associated with this energy level is called the ground term of the spectrum, and corresponds to the normal state of the atom. In contrast with this normal state, the states richer in energy are called excited states. To lift the atom from its ground state into a given excited state a certain work is required, and this is called the excitation energy. The magnitude of the excitation energy can be found directly from the term diagram, because it must be equal to the energy difference between the ground state and the relevant excited state. If we call the ground term T_0 , we obtain the excitation energy to produce the excited state associated with a term T namely :

$$A = h(T_0 - T)$$

As a special case we will now consider the excitation energy for producing the state associated with the term $T = 0$. This is the term on which all the term series converge with increasing current numbers. According to Bohr's theory, this term corresponds to the state of the atom in which an electron is completely removed, i.e. the state of the positive ion. The associated excitation energy is the work required to remove an electron, the so-called ionization energy. Thus Bohr's theory requires that the ionization energy of an atom and the ground term of its series spectrum should be simply inter-related by :

$$A_{ioniz} = hT_0$$

The possibility to check this relationship experimentally by means of an electron-impact test follows from Bohr's theory. The identity of the energy difference between the terms of the series spectrum and of the energy of the atom in its various stationary states, leads to the conclusion that the amounts of energy transmitted during collisions between electrons and atoms can be measured directly, and that phenomena which occur when given amounts of energy are imparted to the atom, can be observed. What can we expect on the basis of Bohr's theory, when electrons of a given velocity collide with atoms? If energy is imparted to the atom during such a collision, the result can only be that the atom will be lifted from its ground state to a stationary state of higher energy.

Hence, only given amounts of energy can be transferred to the atom, and each of the possible energy amounts is equal to the excitation energy of a given excited state of the atom. Hence, according to what we have said above, each possible energy amount should be calculable from the associated series term. Among the excited states of an atom, there is always one state for which the excitation energy is a minimum. Thus, the excitation energy associated with this state represents the minimum amount of energy that can be imparted to the atom as a result of an electron impact. So long as the energy of the colliding electron is smaller than this minimum excitation energy, no energy will be transferred to the atom by this collision, which will be a purely elastic one, and the electron will then lose only the extraordinarily small amount of energy which owing to the conservation of momentum takes the form of kinetic energy of the atom. But as soon as the energy of the electron exceeds the minimum excitation energy, some energy will be transmitted from the electron to the atom by the collision, and the atom will be brought into its first excited state. If the energy of the electron rises further, so that it progressively equals and exceeds the excitation energy of higher excited states, the electron will lift the atom into these higher states by the collision, while the energy quantum transmitted will always be equal to the excitation energy of the excited state. If the energy of the electron finally equals the ionization energy, an electron will be removed from the atom by the collision, so that the atom will be left as a positive ion.

In the experimental investigation of these processes a given energy is usually imparted to the electrons by accelerating them by a given voltage. The energy of an electron after the collision is studied by determining the retarding potential which it can still overcome. Therefore, the excitation energy of a given state corresponds to the potential difference through which an

electron with zero initial velocity has to fall in order to make its energy equal to the excitation energy of the atom. This excitation potential is thus equal to the excitation energy divided by the charge of the electron. The ionization potential is associated with the ionization energy in the same way. The main object of the electron-impact experiments was the measurement of the excitation and of the ionization potentials. The methods used can be divided into three main groups. Those of the first group are similar to the Lenard method we used in our first tests. They are characterized by the fact that the occurrence of non-elastic collisions of given excitation potentials is studied by investigating electrically the resulting phenomena. The phenomena concerned here are the photoelectric release of electrons by the ultraviolet light produced as a result of excitation collisions, and the positive charging of collector electrodes by positive ions in the case of impacts of electrons with energies above the ionizing potential. The improvement made to this method by Davis and Goucher, which made it possible to distinguish between these two phenomena, was of fundamental importance. This consisted of introducing a second wire gauze within a short distance from the collector 'plate. To this gauze a small positive or negative potential respectively as compared with the collector plate was applied. When this potential was positive, then the test equipment operated exactly as in the original Lenard method, i.e. the photo-electrons released at the plate were carried away from the plate, while the positive ions produced as a result of ionizing collisions were drawn on to the collector plate. On the other hand, if a negative potential was applied to the wire gauze, the positive charging up of the plate was prevented, since the photo-electrons were returned to the plate by the electrical field. Instead, negative charging of the plate occurred by the photo-electrons released at the wire gauze. Another way of improving the Lenard method consists in arranging the effective collisions between the electrons and the gas molecules in a field-free space, again by introducing a second wire gauze, so that all the collisions occur at a uniform electron velocity. There, the inelastic collisions occur from a given excitation potential onwards far more sharply. In this way it was possible to determine, not only the lowest excitation potentials but also the higher ones, from kinks in the curve representing the photo-electric current released on the plate as a function of the accelerating potential of the electrons.

The methods of the second group follow closely those which we used first in the case of mercury vapour, where we did not study the phenomena caused by the electron impact, but the primary electrons themselves, in order

to find out whether or not they lost energy during the collision. In its original form this method is particularly suitable for measuring the first excitation potential of metal vapours. Like the Lenard method, this method was modified in such a way that the electric collisions occurred in a field-free space, i.e. at a uniform electron velocity. Here too it was possible to measure the higher excitation potentials. A special version of this method, which has been found particularly useful in the case of the inert gases, consists of measuring the number of electrons with zero velocity after the collisions. This can be the case only when the energy of the electrons before the collision is exactly equal to the excitatron energy of a given stationary state. Hence, a sharply defined peak in the measured curves is obtained for every excitation potential.

Whereas in the first two groups of experimental methods the excitation and ionization potentials were determined by electrical measurements, in the third group of methods we carried out a spectroscopic examination of the light emitted as a result of collisions between electrons and molecules, or so far mostly of collisions between electrons and atoms. The method of observation is that which we used to determine the quantum excitation of the mercury resonance line, and it was refined in exactly the same way as the methods described earlier, by making the collisions take place in a field-free space. Since this method has been used mainly to determine the successive appearance of the individual lines of a spectrum at the corresponding excitations potentials, and not to carry out accurate measurements of excitation potentials, we shall not discuss the results obtained thereby until we have dealt with those obtained with the other methods.

By comparing the values of the excitation and ionization potentials found experimentally, with the values calculated from the series terms, we will now show that extremely good agreement has been obtained in all the cases studied so far. The position is simplest in the case of the alkali metals. Fig. 4 illustrates the series diagram of sodium graphically; the spectra of the other metals of this group are of a similar type. The ground term is the term denoted by $1S$; proceeding from this term to the states of higher energy, we first find two different terms, the energies of which differ very little from each other and which are denoted by 2^2P_1 and 2^2P_2 . The transitions of the atom from the stationary states associated with these terms, to the ground state, are connected with the emission of the so-called resonance lines; in the case of sodium these are the two components of the well-known yellow sodium line. They are called resonance lines because an atom that has been excited through absorption of radiation of the frequency of these lines must;

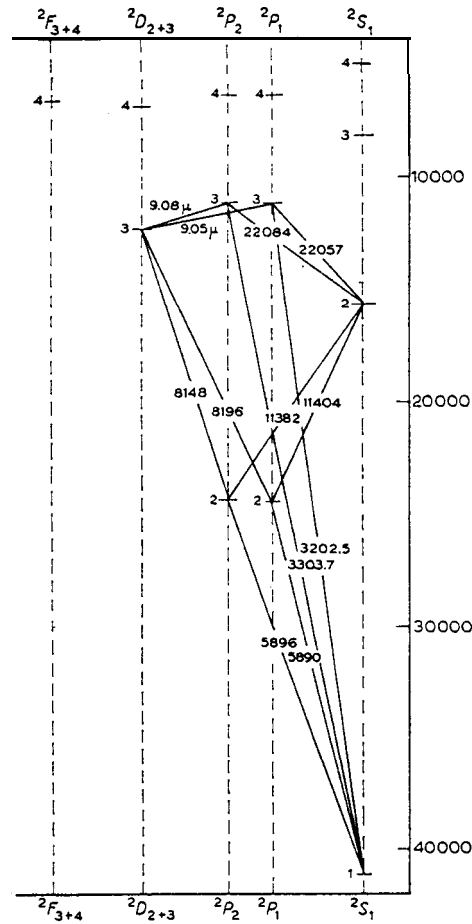


Fig. 4.

on returning to the ground state, emit as radiation of the same frequency, all the energy which it gained by absorption. Hence in relation to the radiation of this frequency, the atom behaves as an electrical oscillator of this characteristic frequency. The first excitation potential V_{exc} of the alkali metals is found, not only as in all the other cases from the difference between the ground term and the next term above it, but, on the basis of Bohr's frequency condition, very simply from the frequency ν_{res} of the resonance line, viz. :

$$V_{exc} \cdot e = h\nu_{res}$$

where e is the charge of the electron. It will be seen from Fig.4 that for

electron impacts leading to this first excitation potential, emission of the resonance lines must take place; hence, the name of resonance potential has been given to this excitation potential of the resonance lines. It should be noted, however, that it is only in the case of the alkali metals that the resonance potential is identical with the first excitation potential. Table 1 compares the spectroscopic data, the data calculated therefrom on the basis of Bohr's theory, and the resonance and ionization potentials observed in electron-impact tests, for the alkali metals. The agreement between the calculated and observed values shows that the conclusions from Bohr's theory are completely verified by the electron-impact tests.

In the case of the metals of the second column of the Periodic Table the spectrum is rather more complicated, because it is made up of two systems, the singlet and the triplet system, as can be seen for example in the diagram of the mercury spectrum shown in Fig. 3. Each of these systems contains a resonance line, in the case of mercury these are the lines 1849 and 2537 Å drawn in the diagram. Here, however, the first excitation potential is not equal to the excitation potential of a resonance line, because there is still another stationary state at a slightly lower energy level than that to which

Table 1.

	Z		ν	λ in Å	Volts	
					Spectroscopic	Electrical
Li	3	1S	43484.45		5.368	
		1S—2P ₂				
		1S—2P ₁	14903.09	6708.2	1.840	
Na	11	1S	41448.59		5.116	5.13 ¹ 5.18 ²
		1S—2P ₂	16955.88	5895.9		
		1S—2P ₁	16973.52	5889.9	2.093	2.12 ¹ 2.13 ²
K	19	1S	35005.88		4.321	4.1 ¹ 4.41 ²
		1S—2P ₂	12985.05	7699.1	1.603	1.55 ^{1,2}
		1S—2P ₁	13042.95	7664.9	1.610	1.63 ⁴
Rb	37	1S	33684.80		4.159	4.1 ³
		1S—2P ₂	12579.01	7947.6	1.553	
		1S—2P ₁	12816.72	7800.2	1.582	1.6 ³
Cs	55	1S	31406.70		3.877	3.9 ³
		1S—2P ₂	11178.4	8943.6	1.380	
		1S—2P ₁	11732.5	8521.2	1.448	1.48 ³

¹ I. T. Tate and P. D. Foote; ² A. Campetti; ³ P. D. Foote, O. Rognley, and F. L. Mohler; ⁴ R. C. Williamson.

the atom is excited by absorption of the longer-wave resonance line. Such a state is called metastable by Franck, because an atom which has reached such a state cannot return to the normal state spontaneously through emission. In the case of mercury, where this initial excitation potential is located 0.22 V below the resonance potential, the separation of the two terms can be proved experimentally. In the other metals of this column of the Periodic Table the difference is only a few hundredths of a volt, so that the two terms cannot be distinguished by the electron-impact method. Table 2, which is similar to Table 1, compares the experimental values with the values obtained from the series terms, for the metals of the second column of the Periodic Table.

In addition to metal vapours, the inert gases are suitable for investigation by the electron-impact method, because they too are monatomic and have no electron affinity. Compared with metal vapours, it is of the great advantage that the inert gases can be examined at room temperature, and this is very important for accurate measurements. Since their excitation potentials are greater than those of all other gases, they are highly sensitive to impurities. Another drawback, especially in the case of the heavy inert gases, is due to the fact that the yield of the excitation collisions is far smaller than that of the metal vapours. Hence, the methods that can be used with metal vapours are more or less unsatisfactory in the case of the inert gases. For example, the method of determining the absolute value of the first initial excitation potential from the distance between successive peaks, cannot be used here. This makes it very difficult to find the absolute values of the excitation potentials. The velocity of the impacting electrons does generally not correspond accurately to the applied accelerating potential. Instead, owing to the initial velocity of the electrons, the potential drop along the hot filament, and any Volta potential difference between the hot filament and the other metal parts of the test equipment, a correction has to be made, amounting to a few tenths of a volt. If, as in the case of the metal vapours, the initial excitation potential can be determined by a method in which this error is eliminated, then the correction is known immediately for the other excitation potentials as well. If this is impossible, then an uncertainty arises; this in fact proved to be very troublesome in the first measurement of the excitation potential of helium. It was only after the excitation potentials of helium had been determined accurately by spectroscopic means, that this gas could be used to calibrate the apparatus, i.e. to determine the correction required. In this way, especially after the introduction of the above-mentioned method, it became possible to measure accurately the excitation and ionization potentials of the other inert gases.

Already our first measurements had indicated that the initial excitation potential of helium was about ∞ V (at the time we erroneously believed that this was the ionization potential). Later and more accurate measurements by Franck and Knipping confirmed this result, they also showed that the true ionization potential is 4.8 V higher than this. Fig. 5 gives the diagram of the helium spectrum as it was known at the time when these measurement were made. The spectrum consists of two series systems, the terms of which do

Table 2.

			ν	λ in $\text{\AA}$	<i>Volts</i>		
Z					Calculated	Observed	
Be	4	1^1S					
		$1^1S-2^3P_1$					
		1^1S-2^1P					
Mg	12	1^1S	61 663.0		7.61	7.75 ¹	8.0 ²
		$1^1S-2^3P_1$	21 869.5	45 71.33	2.70	2.65 ¹	2.65 ²
		1^1S-2^1P	35 050.3	28 52.2	4.32	...	4.42 ²
Ca	20	1^1S	49 304.8		6.08	6.01 ³	
		$1^1S-2^3P_1$	15 210.1	65 72.8	1.88	1.90 ³	
		1^1S-2^1P	23 652.4	42 26.7	2.92	2.85 ³	
Sr	38	1^1S	45 924.31		5.67		
		$1^1S-2^3P_1$	14 502.9	68 92.8	1.79		
		1^1S-2^1P	21 697.66	46 07.5	2.68		
Ba	56	1^1S	42 029.5		5.19		
		$1^1S-2^3P_1$	12 636.6	79 11	1.56		
		1^1S-2^1P	18 060.2	55 35.5	2.23		
Zn	30	1^1S	75 758.6		9.35	9.5 ⁴	9.3 ²
		$1^1S-2^3P_1$	32 500.7	30 76.0	4.02	4.1 ⁴	4.18 ²
		1^1S-2^1P	46 743.6	21 39.3	5.77		5.65 ²
Cd	48	1^1S	72 532.8		8.95	9.0 ²	8.92 ⁵
		$1^1S-2^3P_1$	30 655.2	32 61.2	3.78	3.95 ²	3.88 ⁵
		1^1S-2^1P	43 691.2	22 88.8	5.39	5.35 ²	
Hg	80	1^1S	84 181.5		10.39	10.2 ² 10 ⁶	10.1 ⁷
						10.8 ⁸ 10.3 ⁹	10.4 ¹⁰
		$1^1S-2^3P_1$	39 412.6	25 36.5	4.86	4.9 ²	
		1^1S-2^1P	54 068.7	18 49.5	6.67	6.7 ²	

¹ P. D. Foote and F. L. Mohler; ² F. L. Mohler, P. D. Foote, and W. F. Meggers;

³ F. L. Mohler, P. D. Foote, and H. F. Stimson; ^{4,5} I. T. Tate and P. D. Foote; ⁶ F. M. Bishop; ⁷ C. G. Found; ⁸ G. Stead and B. S. Gossling; ⁹ I. T. Tate; ¹⁰ B. Davis and F. S. Goucher.

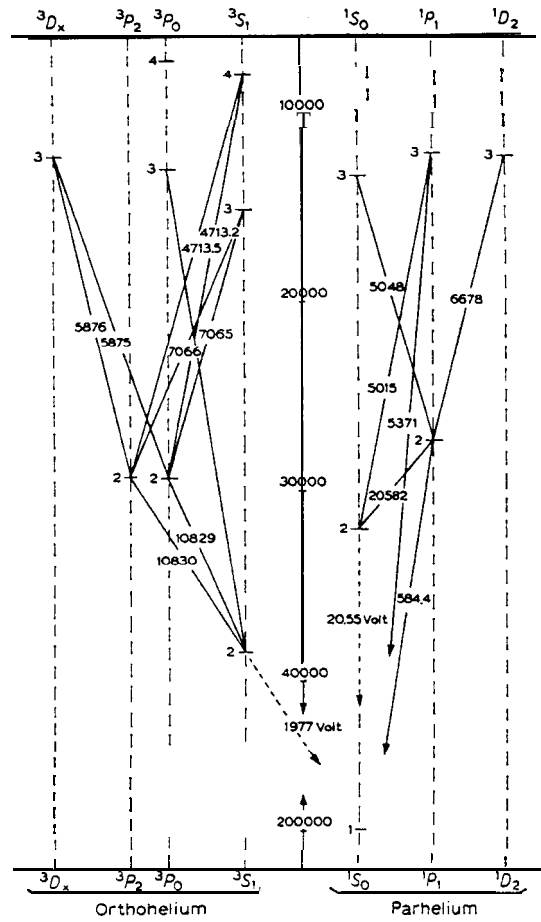


Fig. 5.

not combine with each other. This means that there are two systems of stationary states, having the property that by light emission the atom will always pass from an excited state in one of the two systems, to a state of the very same system. A comparison with the measured values of the excitation and ionization potentials shows immediately that the lowest term of this diagram is not by any means the ground term, though it is the term corresponding to the normal state of the helium atom. This term is not equal to the ionization energy divided by h , but it is equal to the difference between the initial excitation energy and the ionization energy, divided by h . Hence the diagram of helium has to be supplemented by another term, the ground term, which lies about 20 V below the term with the lowest energy

of those previously known. The existence of this term was soon demonstrated by Lyman's spectroscopic measurements of the helium spectrum in the extreme ultraviolet region, when its magnitude was also determined accurately. The resulting values of the critical potentials are: for the initial excitation potential 19.77 V, for the ionizing potential 24.5 V. Franck recognized as metastable the first excited state of helium on the basis of Paschen's observation of resonance fluorescence in electrically excited helium, and thus was the first to demonstrate the existence of atoms in the metastable state.

The other inert gases are also very interesting as regards to the verification of Bohr's theory by means of electron-impact tests. Their excitation and ionization potentials were measured at a time when the spectra in the short-wave ultraviolet region which were required for the spectroscopic determination of these critical potentials, were still unknown. Table 3 illustrates the close agreement between the values of the initial excitation potentials and the ionization potentials measured by the electron-impact method, and the values obtained later from measurements in the short-wave spectrum. Because the time here is not available we have to refrain here from discussing other interesting features of the results.

In the third group of tests, i.e. those in which the radiation produced by electron-collisions was studied in relation to the energy of the colliding electrons by spectroscopic methods, the results appeared for some time to contradict Bohr's theory. In fact, our results concerning the mercury resonance line showed that the impact of electrons with energies immediately above the resonance potential excited the mercury atom to emit this line without the appearance of the other lines, and this was confirmed by a study of the corresponding lines of other metals of the second column of the Periodic

Table 3.

	<i>First excitation potential— measured (volts)</i>	<i>Excitation potential of long-wave resonance line— calculated (volts)</i>	<i>Ionizing potential— measured (volts)</i>	<i>Ionizing potential— calculated (volts)</i>
Neon	16.6	16.60	21.5	21.47
Argon	11.5	11.57	15.4	15.7
Krypton	9.9	9.99	13.3	} still unknown
Xenon	8.3	8.40	11.5	

Table. These investigations, which were carried out mainly by American workers, also showed that the behaviour of the second resonance line was exactly the same. It will be seen directly from the diagram of the mercury spectrum in Fig. 3 (cf. also Table 2), that this line must also appear, as soon as by an increase of the accelerating potential above the excitation potential of the longer-wave resonance line, the excitation potential of the shorter-wave resonance line is reached. The emitted spectrum now contains only the two resonance lines. In Fig. 6, which shows photographs of the magnesium spectrum obtained from excitation by the impact of electrons of various velocities (taken from a work by Foote, Meggers, and Mohler), these two stages

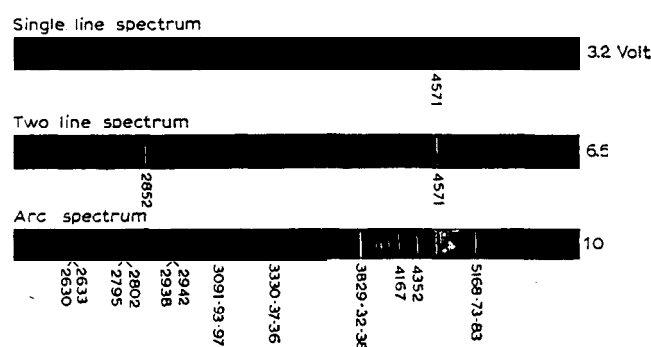


Fig. 6.

are clearly visible. According to Bohr it was expected that on further rise in the velocity of the impacting electrons the other spectral lines would appear in succession at the excitation potentials calculated from the series diagram. Surprisingly, the tests first gave a different result, namely that the higher-series lines all seemed to appear simultaneously once the ionizing potential was exceeded. But it is the behaviour of these higher-series lines which is of greatest importance for the experimental verification of Bohr's theory. In the case of the resonance lines, which correspond to transitions of the atom from an excited state to the normal state of the atom, the excitation potential is determined by the simple relation $V \cdot e = h\nu$; in relation to the emission of a resonance line, the atom thus behaves like a Planck oscillator having the frequency of this line. It is in fact characteristic for Bohr's theory that in the case of the higher-series lines the excitation potential must be calculated, not from the frequency of the line on the basis of the $h\nu$ -relation, but from the series terms in the manner described in detail above. When the tests were

further refined, mainly by eliminating the interference of space charges, the higher-series lines were also found to behave in the manner predicted according to Bohr's theory. As examples to illustrate this behaviour we present in Figs. 7 and 8 photographs of the spectra of mercury and helium which were excited by the impact of slow electrons of various velocities. The wavelengths of the individual lines are given, together with (in brackets) the excitation potentials in volts, calculated from the series terms.

Summarizing therefore, it can be stated that all the results so far attained with the electron-impact method agree very closely with Bohr's theory and in particular that they verify experimentally Bohr's interpretation of the series terms as a measure of the energy of the atom in its various stationary states. We can hope that further applications of this method of investigation will provide more material for testing recent developments of the theory. So

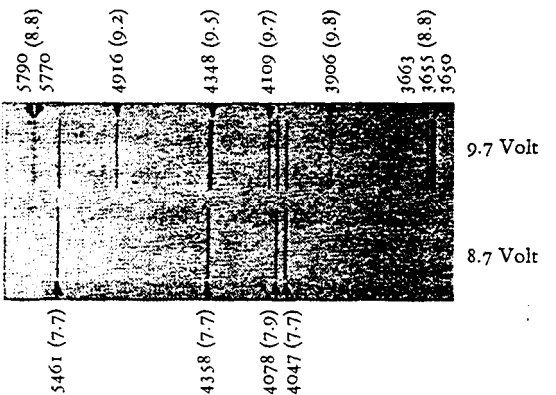


Fig. 7.

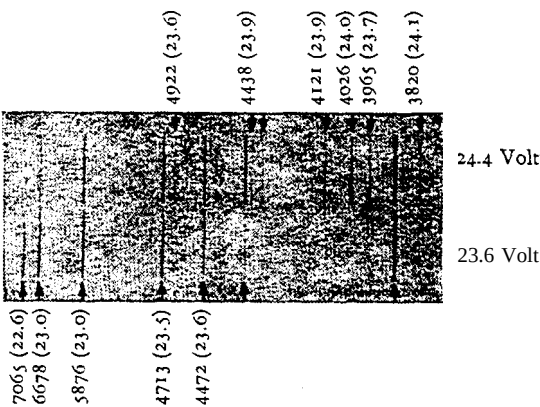


Fig. 8.

far the tests are concerned almost exclusively with the amount of energy transmitted by electron-impact. The next important task consists in the measurement of the yield of non-elastic electron-collisions, i.e. of the probability that in a collision between an electron of sufficient velocity and an atom, energy will in fact be transferred. Exploratory tests in this field have already been made, but no definitive conclusions have yet been reached. Naturally such tests will also lead to a closer investigation of the elastic collisions, and to a study of problems of the mean free path, which have become particularly interesting as a result of Ramsauer's measurements, and of many other problems, so that there is ample scope for further experimental work in this field.

Biography

Gustav Ludwig Hertz was born in Hamburg on July 22nd, 1887, the son of a lawyer, Dr. Gustav Hertz, and his wife Auguste, née Arning. He attended the Johanneum School in Hamburg before commencing his university education at Göttingen in 1906; he subsequently studied at the Universities of Munich and Berlin, graduating in 1911. He was appointed Research Assistant at the Physics Institute of Berlin University in 1913 but, with the onset of World War I, he was mobilized in 1914 and severely wounded in action in 1915. Hertz returned to Berlin as Privatdozent in 1917. From 1920 to 1925 he worked in the physics laboratory of the Philips Incandescent Lamp Factory at Eindhoven.

In 1925, he was elected Resident Professor and Director of the Physics Institute of the University of Halle, and in 1928 he returned to Berlin as Director of the Physics Institute in the Charlottenburg Technological University. Hertz resigned from this post for political reasons in 1935 to return to industry as director of a research laboratory of the Siemens Company. From 1945 to 1954 he worked as the head of a research laboratory in the Soviet Union, when he was appointed Professor and Director of the Physics Institute at the Karl Marx University in Leipzig. He was made emeritus in 1961, and since then he has lived in retirement, first in Leipzig and later in Berlin.

Hertz's early researches, for his thesis, involved studies on the infrared absorption of carbon dioxide in relation to pressure and partial pressure. Together with J. Franck he began his studies on electron impact in 1913 and before his mobilization, he spent much patient work on the study and measurement of ionization potentials in various gases. He later demonstrated the quantitative relations between the series of spectral lines and the energy losses of electrons in collision with atoms corresponding to the stationary energy states of the atoms. His results were in perfect agreement with Bohr's theory of atomic structure, which included the application of Planck's quantum theory.

On his return to Berlin in 1928, it was his first task to rebuild the Physics Institute and re-establish the School, and he worked tirelessly towards this

end. There he was responsible for a method of separating the isotopes of neon by means of a diffusion cascade.

Hertz has published many papers, alone, with Franck, and with Kloppe, on the quantitative exchange of energy between electrons and atoms, and on the measurement of ionization potentials. He also is the author of some papers concerning the separation of isotopes.

Gustav Hertz is Member of the German Academy of Sciences in Berlin, and Corresponding Member of the Göttingen Academy of Sciences; he is also Honorary Member of the Hungarian Academy of Sciences, Member of the Czechoslovakian Academy of Sciences, and Foreign Member of the Academy of Sciences U.S.S.R. He is recipient of the Max Planck Medal of the German Physical Society.

Professor Hertz was married in 1919, with Ellen neé Dihlmann, who died in 1941. They had two sons, both physicists. Dr. Hellmuth Hertz, Professor at the Technical College in Lund, and Dr. Johannes Hertz, working at the Institute for Optics and Spectroscopy of the German Academy of Sciences in Berlin.

Since 1943, Professor Hertz is married with Charlotte, *née* Jollasse.

Physics 1926

JEAN BAPTISTE PERRIN

«*for* his work on the discontinuous structure of matter, and especially for his
discovery of sedimentation equilibrium »

Physics 1926

Presentation Speech by Professor C. W. Oseen, member of the Nobel Committee
for Physics of the Royal Swedish Academy of Sciences

Your Majesty, Your Royal Highnesses, Ladies and Gentlemen.

Nature can be physically explained in two ways. When a group of phenomena is to be understood, we can seek to deduce, on the basis of observations, general laws from which it will be possible to infer concrete phenomena. Or we can proceed from a hypothesis on the structure of matter and seek to explain the phenomena from that. These two methods have been explored so long as physical research has been carried out.

An example will allow me to show the difference between the phenomenological and the atomistic description of Nature. We all know that air is less dense at the top of a mountain than at ground level. This phenomenon is explained completely by the laws which govern a heavy gas, and there is no reason for not considering the gas as a continuous medium. The problem is herewith solved so far as the phenomenological description is concerned. But for the supporters of the molecular theories the results obtained in this way constitute only a superficial description of the phenomena. For him, a gas evokes the image of a multitude of molecules moving in all directions. Only an explanation which reduces the phenomenon to the laws of molecular movements can be satisfactory to him.

The object of the researches of Professor Jean Perrin which have gained for him the Nobel Prize in Physics for 1926 was to put a definite end to the long struggle regarding the real existence of molecules.

The idea which Professor Perrin pursued in the early stages of his researches was this. If it follows from the laws governing the movements of molecules that in spite of its weight air is not compressed against the surface of the earth, but that it extends-while becoming rarefied, it is true-well above the highest mountains, in that case, and seeing that the movements of molecules obey the same laws as every other minute body, there must be something analogous for every system of small bodies. If a large quantity of sufficiently small and light particles is distributed in a liquid, not all of them should yet settle at the bottom even if they are heavier than the liquid, but they should distribute themselves at different levels according to a law similar to that for the air. Perrin, now, had to realize this experiment.

He had for this purpose to prepare a system of very small particles, all of which, moreover, should have the same weight and the same size. He succeeded herein by using gamboge, a preparation obtained from a vegetable sap and which can be handled like soap. By rubbing the gamboge between his hands under water, Perrin obtained an emulsion which under the microscope proved to consist of a swarm of spherical particles of different size. He then succeeded in obtaining from it an emulsion of particles of the desired dimension and all of equal size. This was by no means an easy operation which is proved by the fact that after several months of accurate and careful work Perrin was able to obtain from one kilogram of gamboge only some decigrams of particles of the desired size. It then became possible to undertake the experiment. The result was as expected. By means of his gamboge emulsion Perrin was able to determine one of the most important physical constants, Avogadro's number, that is to say the number of molecules of a substance in so many grams as indicated by the molecular weight, or to take a special case, the number of molecules in two grams of hydrogen. The value obtained corresponded, within the limits of error, to that given by the kinetic theory of gases. Vast work to verify this, has not shaken the soundness of the method.

It may perhaps be said that in the work which we have just summarized Perrin has offered indirect evidence for the existence of molecules. Here, follows a direct evidence. Microscopic particles in a liquid are never at rest. They are in perpetual movement, even under conditions of perfect external equilibrium, constant temperature, etc. The only irrefutable explanation for this phenomenon ascribes the movements of the particles to shocks produced on them by the molecules of the liquid themselves. A mathematical theory of this phenomenon has been given by Einstein. The first experimental proof of this theory was given by a German physicist, Seddig. After him, the problem was taken up by two scientists simultaneously. One of them was Perrin; the other Svedberg. I have to speak of Perrin only. His measurements on the Brownian movement showed that Einstein's theory was in perfect agreement with reality. Through these measurements a new determination of Avogadro's number was obtained.

The molecular impacts produce not only a forward movement of the particles distributed in a liquid, but also a rotational movement. The theory of this rotation was developed by Einstein. Measurements in relation herewith were carried out by Perrin. In these measurements he has found another method for determining Avogadro's number.

What then is the result of these researches? How many molecules are there in two grams of hydrogen? The three methods have given the following answers to this question: 68.2×10^{22} ; 68.8×10^{22} ; 65×10^{22} .

Professor Perrin. For more than thirty years you have worked with your head and your hands in the service of atomistic ideas. Please, accept our congratulations on the result that you have achieved. Allow me also to express the happiness which we experience in greeting you as a representative of the glorious sciences of France. I ask you to receive from the hands of our King the Nobel Prize in Physics for 1926.

J E A N P E R R I N

Discontinuous structure of matter

Nobel Lecture, December 11, 1926

Since I have the great honour to have to summarize here the work which has enabled me to receive the high international distinction awarded by the Swedish Academy of Sciences, I shall speak of the ((discontinuous structure of matter ».

Introduction

A fluid such as air or water seems to us at first glance to be perfectly homogeneous and continuous; we can put more water or less water into this glass, and the experiment seems to suggest to us that the amount of water contained in it can vary by an infinitely small amount, which is the same as saying that water is « indefinitely divisible ». Similarly, a sphere of glass or of quartz, a crystal of alum, are received by our senses as being perfectly continuous, and particularly when we see this alum crystal growing in a super-saturated solution, each of the planes bounding the crystal moves parallel to itself in a continuous manner.

However, this can be taken for granted only up to the degree of subtlety reached by the resolving power of our senses which, for example, would certainly be unable to distinguish between two positions of the crystal face one millionth of a millimetre apart. Beyond the things which our senses separate in this manner, our imagination remains free, and ever since ancient times, just as the philosophers who started from the «full» or the «void»), has hesitated between two hypotheses.

For the former, matter remains continuous : « full », not only (as is reasonable and probable) a little beyond this domain on our scale where our senses make it appear as such, but indefinitely.

For the latter, who were the first atomists, all matter consists of minute grains separated by empty gaps; not any hypothesis has been formulated for the structure of these grains themselves, *atoms*, which were considered as indestructible constituent elements of the Universe.

Lastly, and doubtless always, but particularly at the end of the last century, certain scholars considered that since the appearances on our scale were finally the only important ones for us, there was no point in seeking what might exist in an inaccessible domain. I find it very difficult to understand this point of view since what is inaccessible today may become accessible tomorrow (as has happened by the invention of the microscope), and also because coherent assumptions on what is still invisible may increase our understanding of the visible.

Indeed, increasingly numerous and strong reasons have come to support a growing probability, and it can finally be said the certainty, in favour of the hypothesis of the atomists.

There is, first of all, the familiar observation of solutions; we all say, for example, that sugar and water are present in sugar water, although it is impossible to distinguish the different parts in it. And similarly, we recognize quite simply bromine in chloroform. This can be understood if the bromine and the chloroform are formed respectively by very small particles in continuous movement which can intermingle with one another without losing their individuality. Those elementary constituent particles, those molecules, are probably of the same kind, like articles made in series, for each pure substance (defined by its resistance to the fractionation test) or even more surely for each definite chemical species (experiment proves that it is never necessary to consider a continuous sequence of chemical species), and we come to formulate the molecular hypothesis by saying that for a sufficient magnification any fluid appears to us as formed by molecules in continuous movement which impinge ceaselessly upon one another, and of which there are as many distinct varieties as chemical species can be recognized in the fluid under consideration.

These molecules which exist in the mixtures are not indestructible since they must disappear (or appear) when a chemical reaction causes the chemical species which they constitute to disappear (or appear) ; when a mixture of hydrogen and oxygen explodes to give water, the molecules of hydrogen and oxygen certainly have to disappear at the same time as the water molecules appear. But we know that the decomposition of chemical species, when carried out as far as possible, has led to the experimental definition of a small number of simple bodies which can always be recovered, without any change in their nature, and without loss or gain of mass, from combinations in which they have been introduced. It is then very difficult not to assume that, for example, one and the same substance « exists » in all the chemical

species from which the simple substance hydrogen can be regained and which passes, disguised but indestructible, through our various reactions. Dalton supposed, and this is the essential point of the atomic hypothesis, that this substance is formed by a definite variety of particles which are all identical and which cannot be cut into pieces in the reactions which we can produce, and which for this reason are called atoms. There are, therefore, one or several atoms of hydrogen in each molecule of a hydrogenated chemical species.

The fundamental laws of chemistry which are well known to you and which are laws of discontinuity (discontinuity between chemical species, and discontinuous variation according to the « multiple proportions ») in the composition of species made from the same simple bodies) then become immediately clear: they are imposed solely by the condition that the molecule constituting a compound contains a necessarily whole number of atoms of each of the simple bodies combined in this compound. And I do not need to tell you that if one admits that « analogous » bodies (alkali halides, for example) must have analogous formulae, simple chemical analysis will give for the elements of the same « **family** » the ratios of the weights of the atoms, or « atomic weights »), of these elements.

But in order to pass from one family to another, from hydrogen to oxygen for example, it was necessary to have the gas laws and Avogadro's hypothesis or law which I recall because my researches are based on it: when one of those cases occurs where the ratios of the weights of the molecules of the two compounds are known, it is found that masses proportional to these masses (which must, therefore, contain the same number of molecules) occupy equal volumes in the gaseous state under the same conditions of temperature and pressure. This means that as far as these substances are concerned, equal numbers of heavy or light molecules develop equal pressures at the same temperature and in equal volumes. Since the mass of a molecule, and not its nature, must affect the impact of the molecule upon the wall, I see here a justification (not yet agreed, I must say) of the following proposition known as Avogadro's postulate, or hypothesis:

When gaseous masses, at the same temperature and pressure, occupy equal volumes, they all contain the same number of molecules.

These « **equimolecular** » masses are determined for the various chemical species, as soon as one of them has been chosen. They are called *gram-molecules* when the masses in the gaseous state occupy, at the same temperature and pressure, the same volume as 32 grams of oxygen. The number N of the molecules constituting any gram-molecule is *Avogadro's number*. For each

simple substance the gram-molecule of a compound contains as many *gram-atoms* as the molecule contains atoms of this simple substance, and the gram-atom is the product of the mass of the atom and Avogadro's number N .

In short, if molecules and atoms exist, their relative weights are known to us, and their absolute weights would be known at the same time as Avogadro's number.

You also know how-particularly for understanding substitutions-it was assumed that the atoms of a molecule are held together by *valences* of which each unites only two atoms, a kind of bolt holding rigidly together two bars or protuberances which pre-exist on the two atoms. A new detail is thus introduced here to the concept of the atom, but once this new hypothesis is accepted, the structural formulae can be determined for an enormous number of compounds, and with such success in regard to forecasting the properties that it could be said that the hundreds of thousands of structural formulae set up by the organic chemists constitute just as many arguments in favour of the atomic theory.

These brilliant successes tell us, otherwise, nothing about the absolute weights of the atoms. If they all became at the same time a thousand times smaller, a milliard times smaller, infinitesimal in the mathematical sense of the word, with matter becoming again continuous at each reduction, our chemical laws and our formulae would be unchanged, and the idea of the atom, then driven back infinitely far beyond all experimental reach, would lose its interest and its reality.

It will be noted that the laws of *crystallography*, which are laws of discontinuity just as the fundamental laws of chemistry, lead to similar considerations in regard to the dimensions of an elementary cell which is repeated periodically along the three dimensions of a parallelepipedic lattice and should constitute the crystal which is homogeneous in appearance on our scale. Only in this way can one understand how the symmetries of crystals are solely those of reticular systems (for example, never symmetry axes of the order of 5), and explain at the same time the law of rational indices (a kind of laws of multiple proportions which describe what discontinuities separate the possible faces), a law which requires the three dimensions of the elementary parallelepiped to be in definite ratios. Here again the grain of matter could become infinitely small without the laws having to be changed.

In short, in order really to establish the Atomic Theory, it was necessary to obtain the weights and dimensions of the atoms and not only their ratios.

A remarkably successful attempt to do this was made about fifty years ago by the physicists who created the kinetic theory of gases by assuming that gases are made of elastic molecules which are on the average fairly widely separated from one another so that, between two collisions, each molecule can move in a straight line, the duration of the collision being negligible in relation to that of the free path.

Furthermore, if it is agreed that the pressure of a gas on a wall is solely due to the impacts of the molecules upon this wall, and if we write that this (known) pressure must consequently be numerically equal to the impulse exerted perpendicularly on the wall by the molecules impinging against unit surface in unit time, an equation is obtained which shows the mean velocity of the gas molecules.

It is also known that if, in a gas, a rigid plane is made to slide parallel to a fixed plane at a distance D and with a constant velocity V , each intermediate layer at a distance d from the fixed plane is involved with a velocity equal to $V(d/D)$, and that the fixed and moving planes are drawn in opposite directions by forces (per unit surface) equal to the product of the velocity gradient V/D and a fixed factor for each gas, the latter measuring the viscosity of this gas (at the temperature of the experiment). This is readily understood from the kinetic theory: the unit surface of the fixed plane is drawn in the direction of the movement by a force numerically equal to the total excess impulse received in this direction, this excess being proportional to the number of impinging molecules (in other words, both to the density and to the mean molecular velocity which we can determine), and proportional to the mean excess impulse of each impinging molecule; this individual mean excess is itself proportional to the distance of the layer in which the molecule was at the time of the previous impact, and consequently to the *mean free path*. In this way it is seen how Maxwell was able to deduce this *mean-free path* from the experimental determination of the viscosity.

Now, as Clausius observed, the molecules are all the smaller as the mean free path (now known) becomes greater (if the molecules were reduced to points, they would never collide with one another). And it is seen, therefore, that if the free path is known, it is possible to calculate the *total surface* of the molecules which form a given mass of gas. The *total volume* of these same molecules is probably little different from the volume occupied by this mass if it were solidified. Finally, from two obvious equations we derive both the number and the diameter of the molecules which constitute, let us say, a gram-molecule of the gas.

Depending on the gas, the diameters found in this way are graded between 2 and 5 ten-millionths of a millimetre; and the values found for Avogadro's number are between 40×10^{22} and 120×10^{22} . The uncertainty is largely 100 per cent, both because of the inaccuracy of certain measurements and especially because the calculations have been simplified by making assumptions which can only be approximate. But the order of magnitude is achieved: an atom vanishes in our substance almost as the latter would vanish in the sun

The sequence of reasonings which I have just summarized deserves our profound admiration; however, they were not sufficient to carry conviction owing to the uncertainty which in spite of everything existed not only in the simplifying assumptions (sphericalness of the molecules, for example), but in the very hypotheses on which the reasoning is based. This conviction will without doubt come to life if entirely different paths lead us to the same values for the molecular sizes.

The Brownian movement

Let us consider a liquid in equilibrium: the water contained in this glass, for example. It appears to us homogeneous and continuous, and immobile in all its parts. If we place in it a denser object, it falls, and we know quite well that once it has arrived at the bottom of the glass, it stays there and is unlikely to ascend again « by itself »).

We could have observed this water before it reached equilibrium, and to see how it reached it, at the moment when we filled this glass; then we should have been able to find (by observing the visible indicator dust which was specially mixed with the water) that the movement of the various parts of the water which were coordinated at first in parallel movements, became more and more uncoordinated by scattering in all directions between smaller and smaller parts until the whole appeared completely immobile (nothing prevents us as yet from assuming that this scattering will continue without limit).

It is very remarkable that these so familiar ideas become false on the scale of the observations which we can make under a microscope: each microscopic particle placed in water (or any other liquid), instead of falling in a regular manner exhibits a continuous and perfectly irregular agitation. It goes to and fro whilst turning about, it rises, falls, rises again, without tending

in any way towards repose, and maintaining indefinitely the same mean state of agitation. This phenomenon which was predicted by Lucretius, suspected by Buffon, and established with certainty by Brown, constitutes the *Brownian movement*.

The nature of the grains is not important, but the smaller a grain is, the more violently does it become agitated. There is also complete independence between the movements of two grains, even if they are very close together, which excludes the hypothesis of collective convection produced by the impacts or temperature differences. We are, finally, forced to think that each grain only follows the portion of liquid surrounding it, in the same way that an indicating buoy indicates and analyses the movement all the better if it is smaller: a float follows the movement of the sea more faithfully than a battleship.

We obtain from this an essential property of what is called a liquid in equilibrium: its repose is only an illusion due to the imperfection of our senses, and what we call equilibrium is a certain well-defined permanent system of a perfectly irregular agitation. This is an experimental fact in which no hypothesis plays any part.

Since this agitation remains on an average constant (it would be possible to make this « impression » accurate by measurements), the movement possessed by a part of the liquid does not scatter without limit in all directions between smaller and smaller parts, in spite of what observations made on our scale suggest to us; this spreading does not go beyond a certain limit for which, at each moment, just as much movement is coordinated as becomes uncoordinated.

This is explainable if the liquid consists of elastic grains, and I do not see how it can be understood if the structure is continuous. Moreover, it is seen that the agitation for a given observable particle must increase with the size of the molecules: the magnitude of the Brownian movement, therefore, will probably enable us to calculate the molecular sizes.*

In short, the Brownian movement (an experimental fact) leads us to the hypothesis of the molecules; and we then understand quite well how each particle that is situated in a liquid and is being bombarded ceaselessly by neighbouring molecules, receives shocks which on the whole have all the less

* Similarly, the fact that there exists a definite isothermal radiation for each temperature, and that even a temperature is definable without the energy present in the form of radiation continuously gliding towards colours of increasingly smaller wavelengths, requires a structure to be discontinuous (Planck).

change of coming to equilibrium as the particle becomes smaller, with the result that this particle must be tossed to and fro irregularly.

This applies to absolutely whatever kind of particle. If it has been possible to bring into suspension in a liquid a large number of particles all of the same nature, we say that an emulsion has been produced. This emulsion is stable if the particles in suspension do not stick together when the hazards of the Brownian movement bring them into contact, and if they re-enter the liquid when these hazards bring them against the walls or to the surface. From this two-fold point of view such a stable emulsion is comparable to a solution. It is precisely by pursuing this analogy that I have been able to obtain a simple determination of the molecular sizes.

Extension of the gas laws to emulsions

I must, first of all, recall how the gas laws and particularly Avogadro's law came to be regarded, thanks to Van 't Hoff, as applicable to dilute solutions.

The pressure exerted by a gas on the walls limiting its expansion becomes, for a dissolved substance, the osmotic pressure exerted on semi-permeable walls which allow the solvent to pass, but hold back this dissolved substance. Such is a membrane of copper ferrocyanide which separates sugared water from pure water.

Now, the measurements of Pfeffer show that in fact the equilibrium exists only if there is a certain excess pressure from the side on which the sugar is, and Van 't Hoff has pointed out that the value of this excess pressure or osmotic pressure is precisely that of the pressure which would be exerted, in accordance with Avogadro's law, on the wall of the container containing the sugared water if the sugar present could occupy the entire container alone and in the gaseous state. It is then probable that the same would occur with every dissolved substance, but we do not need to recall the thermodynamic reasoning with which Van 't Hoff justified this generalization nor to make other measurements of the osmotic pressure: Arrhenius has indeed shown that every substance which, in solution, confirms the well-known Raoult laws through its freezing temperature and its vapour pressure, necessarily exerts through this very fact the pressure predicted by Van 't Hoff on every wall which halts it without halting the solvent. In short, the Raoult laws which were established by a very large number of measurements, are logi-

cally equivalent to the law of Van't Hoff which consists in the extension of Avogadro's law to solutions, and we can now say:

Equal numbers of molecules, regardless of the kind, in the gaseous state or dissolved, exert - at the same temperature and in equal volumes - equal pressures on the walls detaining them.

This law applies equally to heavy or light molecules, in such manner that, for example, the molecule of quinine which contains more than one hundred atoms, has neither a greater nor a lesser effect when it impinges against the wall than the light molecule of hydrogen which contains two atoms.

I have thought that it was perhaps valid for stable emulsions with visible grains, in such manner that each of these grains which is agitated by the Brownian movement, counts as a molecule when it collides with a wall.

Let us assume then that we can measure the osmotic pressure which equal grains exert, through their Brownian movement, against a unit of a wall which holds them up and allows water to pass (let us say blotting paper). Let us also assume that we can count these grains in the immediate vicinity of the wall unit, that is to say that we know the «abundance» of the grains per unit volume near this wall unit. This number n also measures the abundance of molecules in any gas (let us say hydrogen) which would exert the same pressure on the walls of the container in which it would be enclosed. If, for example, the osmotic pressure measured is the hundred-millionth of a barye, we shall know that a cubic centimetre of hydrogen under normal conditions (pressure equal to a million baryes) contains 100 million million times n molecules ($10^{14}n$). And the gram-molecule (22,412 c.c. in the gaseous state under normal conditions) will contain 22,412 times more molecules: this number will be *Avogadro's number*.

This is very simple; but how to measure the stupendously weak osmotic pressure that an emulsion exerts?

This will, in fact, not be necessary nor, as we have just explained, will it be necessary to measure the osmotic pressure of a solution to make sure that this solution obeys the gas laws. And it will be sufficient for us to find an experimentally accessible property for emulsions which would be logically equivalent to the gas laws.

I found such a property (1908) by extending to emulsions the fact that is qualitatively well known to you, that in a vertical column of a gas in equilibrium the density decreases as the altitude increases.

Law of the vertical distribution of an emulsion

We all know that air is more rarefied at the top of a mountain than at sea level and, generally speaking, the pressure of air has to diminish as one goes higher since this pressure has then to carry only a smaller part of the atmosphere which applies its weight against the earth.

If we specify this slightly vague reasoning in the Laplace manner, we shall say that each horizontal slice of a gas in equilibrium in a large vertical pump would remain in equilibrium if it were imprisoned between two rigid pistons (which would no longer allow exchange of molecules between this slice and the neighbouring slices of the gas) and these pistons would exert respectively the pressures existing at the lower face and at the upper face of the slice; with the result that, per unit surface, the difference of these pressures is equal to the weight of the gas supported. That is to say that if the thickness dh of the slice is sufficiently small so that the abundance of molecules near the upper face differs little from the abundance n near the lower face, the pressure difference dp between the two faces will be equal to $n\pi dh$, where π denotes the weight of a molecule.

This very simple equation expresses two important facts: first of all, as the abundance n of molecules is proportional to the pressure p at each given temperature, we see that for a column of a given gas (for a given π) and of uniform temperature, the relative reduction of the pressure dp/p , or also the relative reduction of the abundance dn/n which can be said to measure the rarefaction, always has the same value for the same difference in level dh , whatever this level may be. For example, each time that you climb a flight of stairs, the pressure in the air (or the abundance of molecules) is reduced by one forty-thousandth of its value. Adding these effects for each step, we see that at whatever level we were originally, each time we ascend by the same height, the pressure (or the density) in air at a uniform temperature will be divided by the same number; for example, in oxygen at 0° the rarefaction will be doubled for each rise of 5 kilometres.

The other fact which emerges immediately from our equation relates to the weight π of the molecule; for the same value of level dh , the rarefaction dp/p (or dn/n) varies in inverse ratio with the weight of the molecule. Adding here again the effects for each step, we see that in two different gases at the same temperature, the rises producing the same rarefaction are in inverse ratio to the molecular weights. For example, as we know that the oxygen molecule (if it exists, and in accordance with the laws summarized

above) must weigh 16 times more than the hydrogen molecule, it is necessary to rise 16 times higher in hydrogen than in oxygen, i.e. 80 kilometres, for the rarefaction to be doubled.

You can appreciate the influence of the altitude, and of the molecular weight, on the rarefaction by looking at this schematic picture where I have drawn three gigantic vertical test tubes (the highest is 300 kilometers) containing equal numbers of hydrogen molecules, helium molecules, and oxygen molecules. At a uniform temperature the molecules would be distributed as shown in the drawing, being more numerous near the bottom as they increase in weight.

Let us now admit that Avogadro's law applies to emulsions as it does to gases.

We assume, therefore, that we have a stable emulsion made of equal grains which is left to itself at a constant temperature, being only under the influence of its own weight. We can repeat the previous reasoning with the only change that the intergranular space, instead of being void, is now a liquid which exerts on each grain, in an opposite direction to its weight, a push in accordance with Archimedes' principle. Consequently, the effective weight π of the grain to which this reasoning is applied, is its actual weight reduced by this push.

If now our generalization is justified, once the emulsion is in equilibrium it will produce a miniature atmosphere of visible molecules where equal rises will be accompanied by equal rarefactions. But if, for example, the rise in the emulsion to double the rarefaction is a milliard times less than in oxygen, it means that the effective weight of the grain is a milliard times greater than that of the oxygen molecule. It will, therefore, be sufficient to determine the effective weight of the visible grain (which forms links between the magnitudes on our scale and the molecular magnitudes) in order to obtain by a simple ratio the weight of any molecule, and consequently Avogadro's number.

It is in this sense that I carried out my experiments which I was able to do successfully.

I first prepared stable emulsions made from solid (vitreous) spheres of various resins in suspension in a liquid (generally water). This was done by dissolving the resin in alcohol and adding to this limpid solution a large amount of water. The resin is quite insoluble in the water and is then precipitated as microscopic spherules of all sizes. By means of prolonged centrifuging similar to those in which the red blood corpuscles are separated from

the blood serum, it is possible to collect these grains as a consistent deposit which splits up again as a stable emulsion of distinct spherules when it is agitated in the pure water after the supernatant alcohol solution has been removed.

It was then necessary, starting with an emulsion where the grains are of very different size, to succeed in separating these grains according to size in order to have *uniform* emulsions (consisting of equal grains). The process which I used can be compared with fractional distillation: just as, in a distillation, the fractions which come off first are richer in the most volatile constituents, so in a centrifuging of a pure emulsion (spherules of the same substance), the parts which settle out first are richer in coarse grains, and this is a method of separating the grains according to size by proceeding according to rules which it would be unnecessary to elaborate here. It is also necessary to be patient: I treated in my most careful fractionation one kilogram of gamboge and obtained after several months of daily operations a fraction containing several decigrams of grains with a diameter of approximately three-quarters of a thousandth of a millimetre which was appreciably equal to what I had wanted to obtain.

If a droplet of a very dilute emulsion made with such equal grains is allowed to evaporate on the slide under a microscope, the grains are seen, when the evaporation is almost complete (and doubtless as a result of capillary action), to run and join together in regular lines just as cannon-balls in a horizontal row of a pile of cannon-balls.

You can see this on the photograph which is now projected. And you will understand how it is possible simultaneously to obtain a successful centrifuging and to measure the mean diameter of the grain of the emulsion. (Other processes are, moreover, possible.)

On the other hand, there is no difficulty in determining the density of the glass constituting the spherules (several processes : the most correct consists in suspending the grains in a solution which is just so dense that the centrifuging cannot separate the grains).

We then know everything necessary for calculating the effective weight of the grain of the emulsion.

On the other hand, we shall have studied the equilibrium distribution of the emulsion under the action of gravity. For this we imprison a drop of the emulsion in a well-closed dish (evaporation must be impossible) arranged for microscopic observation. The distribution of the grains is at first uniform, but it is found that the grains accumulate progressively in the lower layers

until a limiting distribution is reached with reversible settling or expansion depending on whether the temperature is lowered or raised. There are two possible methods of observation, as shown in the drawing projected here. In one method (the horizontal microscope) the rarefaction of the emulsion is obtained immediately from the height, and the resemblance to a miniature atmosphere is extremely striking, precise measurements being possible from instantaneous photographs. But it is then difficult to give the emulsion a height lower than, shall we say, one millimetre, and the time needed for establishing a permanent state becomes long (several days) which involves complications and difficulties.

In the other method of observation the microscope is vertical, and the emulsion imprisoned between the slide and the cover-glass has now a thickness only of the order of a tenth of a millimetre. We take an objective of high magnifying power and weak focal depth so that a very thin horizontal layer of the emulsion (of the order of 2 microns) is clearly seen, and an instantaneous photograph is taken. We thus have the abundance at a certain level (as an aviator could take the density of air at every level). The abundances at different levels are then compared at our leisure.

The success is complete. Before insisting that it is so, I can show a cinematographic film on which you will see for yourselves the equilibrium distribution of an emulsion formed from spherules which are agitated by the Brownian movement.

The observations and the countings which this film summarizes for you prove that the laws of ideal gases apply to dilute emulsions. This generalization was predicted as a consequence of the molecular hypothesis by such simple reasoning that its verification definitely constitutes a very strong argument in favour of the existence of molecules. In particular, it was necessary - it can be verified effectively, and it is very remarkable - that the various emulsions studied lead, within the limit of the possible errors, to the same value for Avogadro's number. In fact, I changed (with the valuable assistance of Bjerrum, Dabrowski, and Bruhat) the mass of the grains (from 1 to 50), their nature (gamboge, mastic), their density (1.20 to 1.06), the nature of the intergranular liquid (water, strongly sugared water, glycerol in the upper layers of which the grains of mastic, being lighter, accumulated) and lastly the temperature (from -9° to $+60^{\circ}$). My most careful measurements made with an emulsion the rarefaction of which doubled with each rise of 6 microns, gave a value for N of 68×10^{22} .

The accuracy of such determinations, so far of several hundredths, can

certainly be improved: the same does not apply to values obtained from the kinetic theory of gases, because here perfecting the measurements would not diminish the uncertainties inherent in the simplifying assumptions which were introduced to facilitate the calculations.

Non-diluted emulsions

Proceeding then further in tracing the similarities between liquids and emulsions, I was able to show (1913) that a non-diluted emulsion is comparable to a compressed liquid of which the molecules would be visible.

For this purpose it was necessary to determine the osmotic pressure as a function of the concentration when the gas laws cease to be applicable. Let us, therefore, consider a vertical column of emulsion which extends upwards practically without limit. At each level the osmotic pressure can be regarded as supporting the whole of the grains above it, and we shall, therefore, know it by counting all these grains. The emulsion will be imprisoned between two vertical plate glasses only several microns apart so that all the grains can be taken by an instantaneous photograph. The concentration of the grains at each level is, on the other hand, fixed by the known number of grains present in a small known volume near this level. In short, we shall in this way know the pressure corresponding to a known concentration: this will give experimentally the law of compressibility which can then be compared with Van der Waals' law.

Rene Costantin made these measurements under my direction and confirmed that Van der Waals' law applies to emulsions which are already too concentrated to conform to the gas laws. The resulting value for Avogadro's number is 62×10^{22} .

Even Van der Waals' law is no longer suitable for concentrations above 3 per cent, but the compressibility remains measurable, consequently the law of compressibility remains known empirically.

This enables - and this idea was due entirely to René Costantin who died for France in 1915 - a theory of Smoluchovski to be checked on the density fluctuations which the molecular agitation should produce in a liquid in equilibrium. According to this theory, the fluctuation $(n'-n)/n$ in a volume containing accidentally n' molecules whilst it should contain only n if the distribution were uniform, has a mean value which can be calculated if the compressibility of the liquid is known, and which includes Avogadro's number.

For our emulsions of equal grains, considered as fluids with visible molecules, the measurements of osmotic compressibility, carried out as far as a content of 7 per cent, have confirmed Smoluchovski's theory by giving approximately 60×10^{22} for Avogadro's number.

Measurements of the Brownian movement

The equilibrium distribution of an emulsion is due to the Brownian movement, and the more rapidly as this movement is more active. But this rapidity is not important for the final distribution. In fact, as we have just seen, I also studied the distribution first on the permanent state without making any measurement on the Brownian movement. But by means of such measurements it is possible, though in a less obvious manner, to demonstrate the discontinuous structure of matter and to obtain a determination of Avogadro's number.

It is due to Einstein and Smoluchovski that we have a kinetic theory of the Brownian movement which lends itself to verification.

Without being disturbed by the intricate path described by a grain within a given time, these physicists characterize the agitation by the rectilinear segment joining the point of departure with the point of arrival, the segment being on an average greater as the agitation is livelier. This segment will be the displacement of the grain during the time considered.

If we then admit that the Brownian movement is perfectly irregular at right angles to the vertical, we prove that the mean horizontal displacement of a grain is doubled when the duration of the displacement is quadrupled, and is tenfold if that duration becomes a hundredfold, and so forth. This means that the mean square of the horizontal displacement is proportional to the duration t of this displacement. This can easily be verified.

Now, this mean square is equal to twice the mean square $\bar{X}^2$ of the projection of the displacement on an arbitrary horizontal axis. Consequently, the mean value of the quotient $\bar{X}^2/t$ for a given grain remains constant. Obviously, since it increases as the grain is more agitated, this mean quotient characterizes the activity of the Brownian movement.

Having said this, there must be a *diffusion* for the grains of an emulsion just as for the molecules of a solution; Einstein shows that the coefficient of diffusion should be equal to the half of the number which measures the activity of the agitation.

On the other hand, the steady state in a vertical column of emulsion is produced and maintained by the interplay of two opposing actions, gravity and the Brownian movement; this can be expressed by writing that at each level the flow through diffusion towards the poor regions is equal to that which gravity produces towards the rich regions.

In order to calculate the flow by diffusion it must be admitted, as we have done, that grains or molecules are equivalent to each other in regard to the osmotic pressures; in order to calculate the flow produced by gravity, in the case of spherules of radius a , it must be admitted, though at first it appeared uncertain, that the (very weak) mean velocity of fall of a grain animated by a very active Brownian movement can still be calculated by « Stokes' law » which applies to the uniform fall in a viscous liquid of a large sphere which is practically not animated by a Brownian movement. In fact, I have since shown experimentally that this is so.

Having admitted this hypothesis, Einstein finds that the diffusion coefficient $\frac{1}{2} \overline{X^2}/t$ is equal to $(RT/N)(6\pi a z)^{-1}$ (R being the gas constant, T the absolute temperature, and z the viscosity).

So far 'we have thought of the *translational* Brownian movement only. Now a grain rotates at the same time as it is displaced. Einstein was able to show that if $\overline{A^2}$ denotes the mean square in a time t of the component of the angle of rotation around an axis, the agitation coefficient of rotation $\overline{A^2}/t$ is fixed for the same grain and should be equal to $(RT/N)(4\pi a^3 z)^{-1}$. His reasoning implies equality between *the mean energy of translation and the mean energy of rotation* which was predicted by Boltzmann and which we shall make more probable if we succeed in confirming this equation.

These theories can be judged by experiment if we know how to *prepare spherules of a measurable radius*. I was, therefore, in a position to attempt this check as soon as I knew, thanks to Langevin, of the work of Einstein.

I must say that, right at the beginning, Einstein and Smoluchovski had pointed out that the order of magnitude of the Brownian movement seemed to correspond to their predictions. And this approximate agreement gave already much force to the kinetic theory of the phenomenon, at least in broad outline.

It was impossible to say anything more precise so long as spherules of known size had not been prepared. Having such grains, I was able to check Einstein's formulae by seeing whether they led always to the same value

for Avogadro's number and whether it was appreciably equal to the value already found.

This is obtained for the displacements by noting on the camera lucida (magnification known) the horizontal projections of the same grain at the beginning and at the end of an interval of time equal to the duration chosen, in such a manner as to measure a large number of displacements, for example in one minute.

In several series of measurements I varied, with the aid of several collaborators, the size of the grains (in the ratio of 1 to 70,000) as well as the nature of the liquid (water, solutions of sugar or urea, glycerol) and its viscosity (in the ratio of 1 to 125). They gave values between 55×10^{22} and 72×10^{22} , with differences which could be explained by experimental errors. The agreement is such that it is impossible to doubt the correctness of the kinetic theory of the translational Brownian movement.

It must otherwise be observed that although it is didactically of comparable difficulty to the kinetic theory of the viscosity of gases, Einstein's theory does not introduce simplifying approximations and, like the measurement of height distribution, lends itself to a precise determination of Avogadro's number.

My most careful measurements which gave me N equal to 69×10^{22} had been made on grains which, for reasons which are no longer of interest, had their initial position at 6μ from the bottom of the preparation. In the course of the verifications which I had asked René Costantin to make on preparations which were only several microns thick, he found that the vicinity of a wall slowed down the Brownian movement. The measurements made at a distance from the walls gave a value for N of 64×10^{22} .

With regard to the *rotational* Brownian movement, Einstein's formula predicts a mean rotation of approximately 8° per hundredth of a second for spheres of 1μ diameter, a rotation which is too rapid to be perceived and which-with greater reason-escapes measurement. And, in fact, this rotation had not been made the subject of any experimental study, at least not quantitatively. (Einstein did not suppose that his formula could be verified.)

I overcame the difficulty by preparing large spherules of mastic. I arrived at them by making pure water pass slowly under an alcohol solution of resin. A passage zone is produced where the grains form which then have generally a diameter of some twelve microns. They are limpid spheres, like glass balls. They frequently seem to be perfect, and then their rotation is not observable. But they also frequently contain small vacuoles, *guide*

marks by means of which the rotational Brownian movement is easily perceived

But the weight of these large grains keeps them very close to the bottom which disturbs their Brownian movement. I, therefore, tried to give the intergranular liquid the density of the grains by dissolving suitable substances in it. A complication soon arose in that at the amount necessary for keeping the grains suspended between the two waters, almost all these substances agglutinated the grains into *bunches of grapes*, showing thus in the nicest way possible the phenomenon of *coagulation* which is not easy to obtain on ordinary suspensions or colloidal solutions (of ultramicroscopic grains). Coagulation failed to occur in a single substance, urea.

In water containing 27 per cent urea I was, therefore, able to follow the agitation of the grains and to measure their rotation. For this I noted at equal intervals of time the successive positions of certain vacuoles from which it was then possible, at one's leisure, to find again the orientation of the sphere at each of these moments and to calculate its rotation from one moment to the next. The calculations were made on approximately zoo (fairly rough) angle measurements on spheres having a diameter of $13\ \mu$, and gave me for N the value of 65×10^{22} . This agreement with the previous determinations is all the more striking as even the order of magnitude of the phenomenon was not known (1910).

The molecular reality

Briefly, and in spite of the variety of experimental conditions and techniques, the study of the emulsions gave me for Avogadro's number:

- 68×10^{22} by means of the distribution of emulsions analogous to gases;
- 62×10^{22} by means of that of emulsions analogous to liquids;
- 60×10^{22} by means of the fluctuations in concentrated emulsions;
- 64×10^{22} by means of the translational Brownian movement;
- 65×10^{22} by means of the rotational Brownian movement;

or, as a crude average, 64×10^{22} .

I can recall here that on the other hand, considering gases as consisting of molecules which diffract light (Rayleigh, Smoluchovski, Einstein) it was possible to obtain (somewhat after my first experiments) Avogadro's number by means of measurements relating to the *critical opalescence* (Keesom: 75×10^{22}), the *blueness of the sky* (Bauer and L. Brillouin, then Fowler:

65×10^{22}), and relating in a particularly precise manner to light that was laterally diffused by gases (Cabannes: 65×10^{22} ; 1921).

The theory of black-body radiation, where the reasoning is allied to that of the kinetic theory, gives again the same value (64×10^{22}).

Along other lines, the measurements of the electric charges of charged microscopic dust, which should be whole multiples of the elementary charge of ions, led by stages with Townsend, J. J. Thomson, Harold A. Wilson, Ehrenhaft, and finally Millikan (1909)-to the same result (61×10^{22}).

Lastly, radioactivity which enables the atoms forming a given mass of helium to be counted one by one, has given in a totally different manner proofs of the discontinuity of matter by imposing once again the same value (62×10^{22} to 70×10^{22}) on Avogadro's number.

Such a collection of agreements between the various pieces of evidence according to which the molecular structure is translated to the scale of our observations, creates a certitude at least equal to that which we attribute to the principles of thermodynamics. The *objective reality of molecules and atoms* which was doubted twenty years ago, can today be accepted as a *principle* the consequences of which can always be proved.

Nevertheless, however sure this new principle may be, it would still be a great step forward in our knowledge of matter, and for all that a certitude of a different order, if we could perceive directly these molecules the existence of which has been demonstrated.

Without having arrived there, I have at least been able to observe a phenomenon where the discontinuous structure of matter can be seen directly.

Monomolecular films

I encountered this phenomenon (1913) by observing under the microscope small laminae of « soapy water », and in such simple conditions that it is surprising it was not discovered earlier.

You know the properties of *thin laminae*: each ray reflected from such a lamina is formed by the superposition of a ray reflected from the front side of the lamina on a ray reflected from the rear side. For each elementary colour these rays add together or subtract from one another according to a classical formula, depending on whether they are in phase or out of phase; in particular, there is extinction when the thickness of the lamina is an even multiple of one quarter of the wavelength, and there is maximum reflection when it is an odd multiple.

If, therefore, white light strikes a lamina which has a thickness increasing continuously from zero, the reflected light is at first non-existent (black lamina), then weak (grey lamina), then lively and still almost white, becoming successively straw yellow, orange yellow, red, violet, blue (tints of the first order), then again (but with different tints) yellow, red, violet, blue, green (second order); and so on, the reflected colour becoming continuously more complex and more off-white up to the « white of a higher order » (the spectrum is furrowed with black grooves the number of which increases with the thickness of the lamina). All these tints will be present at the same time on a lamina which has not a uniform thickness and which will be black or grey in its thinnest region, straw yellow in a thicker region, red in an even thicker region, and so forth.

It is the same with ordinary soap bubbles, with their magnificent colours. The gradation of these colours seems to us perfectly continuous, from the lowest part of the bubble where the wall is thicker, to its upper part, which thinning progressively, becomes white and then grey, after passing through the « first-order » tints. At that moment, just before the bubble bursts, this thin region: begins to show one or several **black spots**, quite round, which contrast strongly with the neighbouring grey tone (I mistook them for holes when I was a child) and the very sharp edge of which marks a strong discontinuity in the thickness. In fact, they are not completely black, but reflect so little light that their thickness is certainly small in relation to the wavelengths of white light. In an enclosed space that is free from dust, these black spots may extend over areas of the order of one square decimetre, and remain for several months (Dewar).

A more careful examination has long since shown that in the first black spot may form even blacker circles, therefore thinner ones, again with a sharp periphery. In measurements which were at the time very remarkable, although not very accurate, Reinold and Rücker, and then Johonnott had shown that the darkest spot could have a thickness of 6 m μ (milli-microns), and the other roughly twice this. No interpretation had been given: it was simply thought that the surface tension which is variable below a certain thickness, became equal again for the thickness of the two black spots to what it is for large thicknesses. In the light of subsequent observations we shall understand that the black spot represents a kind of carpet formed by two layers or perhaps even by a single layer of molecules held together parallel with one another.

Without indicating here the intermediate stages which I passed through,

let us say straightaway that, by observing in the microscope in bright light a small horizontal lamina of a given soapy water (approximately 5 per cent pure alkali oleate), I have seen the discontinuities multiplying of which the black spots were the first example.

The observation is made as for a metal surface: the light emitted through a lateral aperture in the tube of the microscope and reflected towards the objective, passes it and is reflected on the thin lamina, returning to the eye through the objective and the eye-piece to give a clear image of the lamina.

We then see, first of all, the colours in continuous gradation of the ordinary laminae of soapy water; then the lamina quivers; liquid gathers together in globules; at the same time, uniform bands, with flat tints separated from one another by arcs of a circle, appear in the whole lamina which becomes a kind of mosaic. These arcs terminate at the globules around which they radiate like stars. Once this stratification is organized, a very slow evolution takes place by displacement of the contours and the globules, giving (according to circumstances over which I had no control) more or less importance to one band or the other or a series of bands which is the reason for the extraordinary variety of stepped laminae which are observed. Very frequently kinds of flat bulges are seen protruding from the globules or from the non-stratified peripheral liquid and spreading over bands which have already formed.

We thus observe, in order of increasing thickness, black bands which do not seem to differ from the « black spots » which we just mentioned; then grey, white, yellow, red, blue bands; and then bands having second-order tints, and so on, up to higher-order white. Each band has a uniform colour standing out clearly and discontinuously against adjacent bands. The richness of the colours can be extreme as you see from the colour photographs (Lumiere autochrome plates) which are here projected. The richness pertaining partly to a transitional tint - e.g. some purple-represented by an insignificant region on a lamina of ordinary soap, may extend here as a flat tint over an important area.

These bands are definitely liquids; this is shown by the existence of exactly circular contours (when solidification occurs, the areas become like dried skins with a dentated contour), by the mobility of these contours which change by blowing without breaking the lamina, by the existence finally of a ((two-dimensional)) Brownian movement which is found (for droplets, or for small flat discs, pieces detached from the bands), on grey or coloured bands (the Brownian movement is all the less lively when these bands are

thicker which is natural in view of the fact that the frictions then become more important).

Let me add that I have also been able to obtain such stepped laminae with alkali oleate in glycerol, and also with alkali colophonates and resinates in water.

Having examined a large number of stratified laminae, it occurred to me, before I made any measurement, that the difference in thickness between two adjacent bands cannot fall below a certain value and that this elementary minimum difference, a kind of « step of a staircase »), is included a whole number of times in each band. Similarly, if we throw playing-cards on the table, the thickness at each point is that of a whole number of cards, without all possible thicknesses being necessarily present, since two or three cards may remain stuck together. The stratified liquid strips would, therefore, be formed by the piling up of identical sheets, more or less overlapping each other, their liquid state imposing on the free contours the form of arcs of a circle (which are fixed at their extremities on globules or on the non-stratified periphery, according to conditions so far unknown).

The measurements confirmed this impression. From 1913 onwards I found a value ranging between 4.2 and 5.5 μ . And since then, precise photometric determinations made under my direction in 1921 by P. V. Wells, who otherwise had to overcome serious experimental difficulties, have fully established what we can call a law of multiple thicknesses.

We first of all applied simply the classical relationship between the thickness of the lamina and the intensity of the reflected light, using monochromatic lighting.

On the first-order band 120 measurements were made, giving thicknesses grouped according to the law of chances around 4.4 μ . It is certainly the best measurement made so far of the thickness of the « black spot » for which Johonnott gave 6 μ . The extreme thinness of this band, the faintness of the reflected light, and the difficulties due to parasitic lights make this determination particularly interesting.

The set of the measurements for the first fifteen bands give similarly thicknesses which are, within several hundredths, of the successive multiples of 4.5 μ .

As this elementary thickness is not known with a precision greater than 4 per cent, it seems impossible to verify the law above a certain thickness. For example, at this accuracy any thickness greater than 120 μ would be

a multiple of 4.5 m μ . But if the law exists, the thickness should always vary in the same way between two adjacent areas; or again the « step of the stairs » should remain the same, and this can be verified.

This is, in fact, what Wells saw, operating this time in white light and using a method which René Marcelin had suggested to me in 1914, by obtaining tints identical to those of the lamina by means of a quartz compensator of variable thickness which was placed between crossed nicols. (The difference between the thicknesses of quartz which gave the tints of the two adjacent liquid bands, determines the difference in thickness of these bands.) He obtained in this way 4.2 m μ near the first-order violet and 4.3 near the second-order violet.

In short, the « step of the staircase » has the same value near the first, the fiftieth or the hundredth band, i.e. approximately 4.4 m μ ; and we can be sure that:

In a stratified liquid lamina the thickness of each band is a whole multiple of the same elementary thickness;

in other words, it is very probable that:

The bands of the stratified laminae are formed by the overlapping, in any number, of identical fundamental « sheets ».

This is how a « discontinuous and periodic structure » of matter is perceived quite directly, at least in a certain group of cases.

Similar experiments, suggested precisely by these observations of stratified laminae of soapy water, were made on mica at the beginning of 1914 by René Marcelin (who died for France in 1914). We know that if we pour selenium on to mica, and if we try to tear off this mica, thin laminae of mica remain adhering to the selenium. These laminae exhibit bright colourations which are divided into completely flat tints separated by clear rectilinear contours which mark discontinuities of thickness. The minimum difference of thickness measured with the Michel Levy comparator was found to be equal to 0.7 m μ which would, therefore, be the thickness of a monomolecular layer in the crystal. But the measuring accuracy becomes low for such a small thickness.

Let us return to the stratified laminae of soapy water for which the size of the discontinuities is such that we have readily accessible the elementary sheet the periodic repetition of which forms the bands. We shall want to know what this elementary sheet is. I see in it a monomolecular film of hydrated bioleate.

We know, in fact (Rayleigh, A. Marcelin Langmuir) that water on which

float globules of oleic acid, is covered between these globules with a veil of oleic acid 1.9 m μ thick. According to its known density, this veil can be formed only by a single layer of molecules arranged perpendicularly to the surface and probably glued to the water by their (hygroscopic) acid groups. The surface of a soapy water is greasy (low surface tension, arrest of the movements of camphor) ; it is, therefore, covered at least by a similar layer of oleic acid or oleate, as can be shown by analysing a known quantity of soapy water drawn in the form of laminae having a known total surface area (Jean Perrin, Mouquin). The black spot corresponding to the maximum possible thinning would, therefore, be a kind of sandwich containing a layer of water molecules against each side of which, and glued to it by their acid groups, parallel molecules of oleic acid or oleate are arranged, the whole forming an anisotropic lamina or liquid crystalline sheet. The piling-up of such sheets, easily sliding over each other-with weak cohesion forces existing between them-would give the successive bands.

In remarkable agreement with this conception is the fact that the molecular length as calculated for oleic acid from X-ray diffraction measurements recently made in the laboratories of Bragg and Friedel agrees with the thickness of our fundamental sheet.

I do not think that there is any more to be said, at the moment, on the direct visibility of molecules.

The discontinuous structure of the atom

Even whilst evidence continued to accumulate on the still disputed atomic reality, a start was made to penetrate the interior structure of these atoms, a research in which Rutherford and Bohr obtained marvellous results, as we know. And I must summarize here my contribution to this research.

It was known that when an electric discharge passes in a glass tube through a sufficiently rarefied gas, the part facing the cathode is illuminated by a fluorescence on which the shadow of any obstacle placed in front of the cathode is outlined; and that the *cathode rays* definable in this way, are deflected by the magnetic field, describing a circular trajectory when they are thrown at right angles to a uniform field (Hittorf). Crookes had had the intuition that these rays were trajectories of negative particles emitted by the cathode and violently repelled by it (1886), but he did not succeed in establishing this

electrification. And this emission theory was abandoned when Hertz on the one hand failed in his attempts to manifest the negative electricity of the rays, and on the other hand showed that they were able to pass through glass foil or aluminium foil several microns thick. It was assumed since then that the *cathode rays* were immaterial and had a wave-like nature similar to light. This opinion was held principally by Lenard (1894) who showed that these rays can leave the tube where they are formed, through a « window » made of a fairly thick foil to support the atmospheric pressure, and that they can be studied in this way in any gas or in an absolute vacuum.

It seemed to me, however, that the electrified projectiles imagined by Crookes *might differ sufficiently, in size and in velocity, from ordinary molecules, to pass through walls which were impermeable to these molecules*, and seeking to apply without complication the very definition of the electric charge, I made cathode rays penetrate into a « Faraday cylinder » contained inside a protective chamber. As soon as the rays (which can, first, be drawn aside by a magnetic field which is just strong enough to do so) enter the cylinder, the latter presents phenomena which give precisely the definition of a negative electric charge, and which enable it to be measured (1895). This experiment was successful even when the protective chamber was entirely closed, the rays penetrating it through a thin metal foil. Almost at the same time I showed (1896) that cathode rays are deflected by an electric field, and that there is a method here for measuring the drop in potential which had until then been unknown and from which they obtained their energy.

These experiments were at once repeated, and confirmed, by Lenard himself (whose theory they ruined), by Wiechert, by Wien, and by J. J. Thomson.

I had begun to make measurements which were intended to give the velocity (obviously variable according to the circumstances) of the cathode projectiles and the e/m ratio of its charge to its mass, supplementing the measurement of the drop in potential with that of the magnetic field capable of producing a given deflection. I was anticipated here by J. J. Thomson who in the very paper in which he published the confirmation of my experiments showed that once the electrification of the rays had been demonstrated, it was easy to obtain the velocity and the charge of the projectiles from the action of the electrical field and the magnetic field. He found that the e/m ratio, independently of all the circumstances, is approximately 2,000 times greater than it is for hydrogen in electrolysis, and consequently he had the honour of proving that the cathode projectile is much lighter than the hy-

drogen atom (1897). The experimental idea of the electron as a universal sub-atomic constituent was therefore reached, and my experiments had played a certain part in this growth of our knowledge of the manner in which matter is discontinuous.

The problem of the structure of the atom was immediately raised as it ceased to be the ultimate unit of matter. J. J. Thomson assumed that whilst the atom as a whole was neutral, it consisted of a homogeneous sphere of positive electricity inside which the electrons were held in such positions that the attractions and repulsions were in equilibrium.

I was, I believe, the first to assume that the atom had a structure reminding to that of the solar system where the « planetary » electrons circulate around a positive «Sun», the attraction by the centre being counterbalanced by the force of inertia (1901). But I never tried or even saw any means of verifying this conception. Rutherford (who had doubtless arrived at it independently, but who also had the delicacy to refer to the short phrase dropped during a lecture in which I had stated it) understood that the essential difference between his conception and that of J. J. Thomson was that there existed near the positive and quasi-punctual Sun, enormous electrical fields as compared with those which would exist inside or outside a homogeneous positive sphere having the same charge, but embracing the whole atom.

The result was that if a positive charge which is itself quasi-punctual, is sufficiently fast to be able to pass near such a nucleus, it will be strongly deflected just as a comet can be deflected when it comes from the infinite and passes near the Sun. It was in this way (1911), that Rutherford discovered and explained that certain rays (rays described by helium atoms projected by radioactive substances) undergo very strong deflections when they pass through a thin film, producing on a phosphorescent screen, really far from the mean impact of the bundle of rays, scintillations which mark their individual arrivals. All these deflections are explained quantitatively on condition that the *nucleus* is credited with a charge such that the number of planetary electrons is equal to the atomic number » of the atom in Mendeleev's series. In this way each atom consists of an unimaginably small positive nucleus where almost the entire mass of the atom is concentrated and around which the planetary electrons, the presence of which determines the physical and chemical properties of the corresponding element, revolve at relatively colossal distances.

The nucleus itself, lastly, has been revealed as being discontinuous and com-

posed of hydrogen nuclei, or *protons*, which are possibly « cemented » by nuclear electrons.

As Prout had predicted, each atom can, in fact, be regarded as resulting from the condensation on a whole number of hydrogen atoms (the deviating elements having proved to be mixtures of *isotopes*, which confirm the law separately); the small differences which exist are explained (by applying Einstein's law of the mass of energy) by the large variations of internal energy which may accompany these condensations (Langevin). And I have pointed out (1920) that the loss of energy which must then accompany the condensation of hydrogen into helium suffices alone to account for approximately one hundred milliard years of solar radiation at the present rate (the first theory to allow the understanding of the stupendous antiquity of climatic conditions only slightly different from the present conditions: the Helmholtz-Kelvin theory explained only a maximum of 50 million-years, a grossly insufficient figure as far as geology is concerned].

This led me to think that the atoms of hydrogen, and then of helium (the only ones revealed by spectrum analysis in the non-resolvable nebulae) condense progressively, in the course of stellar evolution, into heavier and heavier atoms, radioactive disintegration being the exception and atomic integration being the rule.

However, Rutherford succeeded in proving, in admirable experiments (1922), that when a nucleus of nitrogen, aluminium, or phosphorus is struck forcefully by an a projectile (sufficiently fast to « hit » it in spite of the electrical repulsion), a proton is expelled (a ray) with an energy which may exceed that of the a projectile, and Rutherford interpreted this *transmutation* as being the effect of an explosive disintegration (similar to that of a shell which is exploded by an impact). I maintained, on the contrary (1923), that there was then an integration, that the helium nucleus at first combines with the nucleus that it has hit, to form a radioactive atom (of a species as yet unknown) which soon expels a proton, and that there finally remains an atom which is three units heavier than the atom that has been hit. This has since been confirmed by Blackett (1925) in the very laboratory of Rutherford: three converging rays are counted (by the method of C.T.R. Wilson) when a Rutherford transmutation occurs, instead of the four which would exist if the striking projectile retained its individuality after the impact.

But this refers rather to the evolution of Matter than to its discontinuity; if I were to say any more, I should be departing from the subject on which I came here to speak.

Biography

Jean Baptiste Perrin was born in Lille, September 30, 1870, where he was educated at the École Normal Supérieure, becoming an assistant in physics during 1894-1897, when he began his researches on cathode rays and X-rays. He received the degree of « docteur ès sciences » in 1897 for a thesis on cathode and Röntgen rays and was appointed, in the same year, to a readership in physical chemistry at the Sorbonne, University of Paris. He became Professor here in 1910; a post which he held till 1940, when the Germans invaded his country.

His earliest work was on the nature of cathode rays, and their nature was proved by him to be that of negatively charged particles. He also studied the effect of the action of X-rays on the conductivity of gases. In addition, he worked on fluorescence, the disintegration of radium, and the emission and transmission of sound. The work for which he is best known is the study of colloids and, in particular, the so-called Brownian movement. His results in this field were able to confirm Einstein's theoretical studies in which it was shown that colloidal particles should obey the gas laws, and hence to calculate Avogadro's number N , the number of molecules per gram molecule of a gas. The value thus calculated agreed excellently with other values obtained by entirely different methods in connection with other phenomena, such as that found by him as a result of his study of the sedimentation equilibrium in suspensions containing microscopic gamboge 'particles of uniform size. In this way the discontinuity of matter was proved by him beyond doubt: an achievement rewarded with the 1926 Nobel Prize.

Perrin was the author of many books and scientific papers. His book *Les Atomes*, published in 1913, sold 30,000 copies up to 1936. His principal papers were: « Rayons cathodiques et rayons X » (Cathode rays and X-rays), *Ann. Phys.*, 1897; *Les Principes* (The principles), Gauthier-Villars, 1901; « Électrisation de contact » (Contact electrification), *J. Chim. Phys.*, 1904-1905; « Réalité moléculaire » (Molecular reality), *Ann. Phys.*, 1909; « Matière et Lumière » (Matter and light), *Ann. Phys.*, 1919; « Lumière et Reaction chimique » (Light and chemical reaction), *Conseil Solvay de Chimie*, 1925.

Many honours were conferred on him for his scientific work; the Joule Prize of the Royal Society in 1896, the Vallauri Prize of Bologna in 1912 and, in 1914, the La Caze Prize of the Paris Academy of Sciences.

He held honorary doctorates of the Universities of Brussels, Liege, Ghent, Calcutta, New York, Princeton, Manchester, and Oxford. He was twice appointed a member of the Solvay Committee at Brussels in 1911 and in 1921. He held memberships of the Royal Society (London) and of the Academies of Sciences of Belgium, Sweden, Turin, Prague, Rumania, and China. In 1923 he was elected to the French Academy of Sciences. He became a Commander of the Legion of Honour in 1926, and was also made Commander of the British Empire and of the Order of Leopold (Belgium).

Perrin was the creator of the Centre National de la Recherche Scientifique, an organization offering to most promising French scientists-whose scientific talents would otherwise be lost-a career outside the University. It was due to this institute that Frederic Joliot could carry out his magnificent investigations. In addition to this, he founded the Palais de la Découverte (Palace of discovery) ; he was also responsible for the establishment of the Institut d'Astrophysique, in Paris, and for the construction of the large Observatoire de Haute Provence; without his prestige and his power of persuasion the Institut de Biologie Physico-Chimique would never have come into being.

Perrin was an officer in the engineer corps during the 1914-1918 War. When the Germans invaded his country in 1940 he escaped to 'the U.S.A., where he died on the 17th of April, 1942. After the War, in 1948, his remains were transferred to his fatherland by the battleship Jeanne d'Arc, and buried in the Pantheon.

Physics 1927

ARTHUR HOLLY COMPTON

«for his discovery of the effect named after him»

CHARLES THOMSON REES WILSON

*«for his method of making the paths of electrically charged particles visible by
condensation **of vapour**)*

Physics 1927

Presentation Speech by Professor K. M. G. Siegbahn, member of the Nobel Committee for Physics of the Royal Swedish Academy of Sciences

Your Majesty, Your Royal Highnesses, Ladies and Gentlemen.

The Royal Academy of Sciences has awarded this year's Nobel Prize in Physics to Professor Arthur Holly Compton of the University of *Chicago* for the discovery of the phenomenon named after him the Compton effect, and to Professor Charles Thomson Rees Wilson of the University of Cambridge for his discovery of the expansion method of rendering visible the tracks of electrically charged particles.

Professor Compton has won his prize by work in the field of X-radiation. Soon after Rontgen's discovery it became known that matter exposed to X-rays emits radiations of different character. Besides an emission of electrons, corresponding to the photoelectric effect known also in the optical region of radiation, there is also a secondary X-radiation. Even before the methods of X-ray spectrometry were known, these secondary X-rays were proved by the investigation of their absorption to be of a twofold nature. It was Barkla who, through his fundamental researches, proved that the secondary X-radiation consists partly in a scattering of X-rays, which he thought to have the same penetrability as the original radiation, and partly in a specific X-radiation which was characteristic of the chemical atom and which was more easily absorbed.

When X-rays fell upon matter with small atomic weight, as for example graphite, Barkla was not able to detect the mentioned characteristic X-radiation, but only a scattering; and consequently the secondary rays ought to have the same properties as the original X-rays. Barkla, however, in the course of his investigations of the absorption, had already been able to show that in this case also the secondary X-rays - at least partly -are more easily absorbed than the original radiation and therefore have a greater wavelength. Barkla thought this to be a new characteristic X-radiation.

This is the point where Compton comes in and affects the development of science. He made exact spectrometrical investigations of the secondary X-radiation from matter with small atomic weight: in other words, he undertook to investigate exactly the scattered X-radiation. After some preliminary

work, he found an experimental method that gave results which were as exact as they were astonishing.

Using homogeneous X-rays - corresponding optically to monochromatic illumination, that is to say, to the use of a source of light that emits only one single spectral line - he found that the scattered radiation consists of two lines, one exactly the same as that of the source of rays, the other with a somewhat greater wavelength. This is the first evident manifestation of the Compton effect. Its reality was at first disputed, but of late years it has been well established and verified.

The change in wavelength soon proved to be independent of the nature of the matter used for scattering, while it varies with the angle between the incident and the scattered rays. Hence the phenomenon cannot be explained as a new characteristic radiation of the same nature as that hitherto known; and Compton deduced a new kind of corpuscular theory, with which all experimental results showed perfect agreement within the limits of experimental error.

According to this theory, a quantum of radiation is re-emitted in a definite direction by a single electron, which in so doing must recoil in a direction forming an acute angle with that of the incident radiation. In its mathematical dress this theory leads to an augmentation of the wavelength that is independent of the wavelength of the incident radiation and implies a velocity of the recoil electron that varies between zero and about 80% of the velocity of light, when the angle between the incident and the scattered radiation varies between zero and 180° .

Thus this theory predicts recoil electrons with a velocity generally much smaller than that of the above-mentioned electrons which correspond to the photoelectric effect. It was a triumph for both parties when these recoil electrons were discovered by Wilson's experimental method both by Wilson himself and, independently, by another investigator. Hereby the second chief phenomenon of the Compton effect was experimentally verified, and all observations proved to agree with what had been predicted in Compton's theory.

Quite apart from the improvements and additions that have been made to this theory by other investigators, the Compton effect has, through the latest evolutions of the atomic theory, got rid of the original explanation based upon a corpuscular theory. The new wave mechanics, in fact, lead as a logical consequence to the mathematical basis of Compton's theory. Thus the effect has gained an acceptable connection with other observations in the sphere of

radiation. It is now so important that, in the future, no atomic theory can be accepted that does not explain it and lead to the laws established by its discoverer.

Finally, the fact deserves to be emphasized that the Compton effect has proved to be of decisive influence upon the absorption of short-wave electromagnetic - especially radioactive - radiation and of the newly discovered cosmic rays.

Professor Compton. Your discovery of the phenomenon known as the Compton effect has already proved so important that the Royal Academy of Sciences has awarded you a Nobel Prize, which I now ask you to receive from the hands of His Majesty.

Professor Wilson has been awarded his prize for the discovery of a purely experimental method, which dates back from as long ago as 1911. It is based upon the formation of clouds, which develop when sufficiently moist air is suddenly expanded. The refrigeration caused by the expansion brings the temperature to sink below the dew-point, and the vapour is condensed into small drops, which form together visible clouds. In the first stage of condensation a droplet is always formed round a nucleus. The fact that an electrically charged particle acts as a nucleus in the formation of drops could, after the discovery of the corpuscular radiations, be concluded from an experiment that Helmholtz had, long before, made when he found that a stream of vapour loses its transparency in the vicinity of electrically charged objects.

After it had become known that electricity is conducted through gases by means of ions, and that ions are formed - or, in other words, gases are ionized - under the influence of X-rays or radioactive substances, the way lay open for Wilson to follow photographically the formation of droplets around electrically charged particles. Alpha and beta particles emitted by radioactive substances ionize the gases, and their tracks are marked by a formation of droplets. A suitable photograph of these droplets then gives a picture of the tracks of the ionizing particles.

The problem is a little more complicated when the nature and the details of the ionization caused by X-rays have to be analysed; and the perfect method for such investigations was not described until in a paper of 1923. The extremely delicate regulation of small-time intervals which is necessary in such researches is attained by the use of three pendulums of adjustable period,

which are all released simultaneously. The pendulum which comes down first, opens a communication with a vacuum, and the resulting suction is used, by a mechanical device, to produce a sudden expansion of the gas that is being examined. The second pendulum releases an electric spark, which passes through an X-ray tube, oscillatory sparks being excluded; and thus the anticathode is brought to send an X-radiation of extremely short duration through the gas before the lenses of a stereoscopic camera. The third pendulum releases another electric spark, which passes through mercury vapour and momentarily illuminates the clouds. By means of sliding weights on the different pendulums, just as on an ordinary metronome, Wilson was able to bring it about that the X-rays were sent through the gas at the moment when the expansion was complete, and the illuminating spark just as long afterwards as was needed for a sufficient formation of droplets round the ions, but before the droplets had time to be dislocated by currents in the gas, which might have deformed the tracks visible on the photographic pictures.

Wilson's method attracted attention at first mainly as an elegant and popular method of demonstration. The formation of droplets by α -particles is so dense that the resulting cloud photographs show continuous white lines : and everybody was glad to recognize on these lines the sharp bendings which correspond to the sudden change of direction previously known. Along the β -rays, on the other hand, are seen isolated droplets, and their tracks show a multitude of different types according to differences in initial velocity. For the investigation of such rays with a comparatively small velocity, the most suitable method is the excitation by the momentary X-radiation described above. Here there has been collected a very large photographic material, from which probably not all possible conclusions have yet been drawn, and to which Wilson has devoted assiduous work.

Of late years, new and scientifically important results have been attained which could not have been gained by other methods. The consequence of this is that the discovery, although it was made so long ago, satisfies the provisions for the award of the Nobel Prize. It would not be of much use to describe these results on this occasion, as the understanding of them presupposes full knowledge of the structure of the atom. I will merely call to mind that in 1923 Wilson gave the experimental proof of the existence of the recoil electron tracks that had been postulated by Compton for his explanation of the change in wavelength of scattered X-rays, and that his method has rendered possible the closer examination of these tracks.

Professor Wilson. Although a long time has elapsed since you discovered your elegant expansion method, the high value of your discovery has been greatly augmented both through your own assiduous investigations and through results obtained by others. The Academy is happy that an article in the Statutes allows it in such cases to reward even discoveries of comparatively old date; and I now ask you to receive the prize that you have won from the hands of His Majesty.

ARTHUR H. COMPTON

X-rays as a branch of optics

Nobel Lecture, December 12, 1927

One of the most fascinating aspects of recent physics research has been the gradual extension of familiar laws of optics to the very high frequencies of X-rays, until at the present there is hardly a phenomenon in the realm of light whose parallel is not found in the realm of X-rays. Reflection, refraction, diffuse scattering, polarization, diffraction, emission and absorption spectra, photoelectric effect, all of the essential characteristics of light have been found also to be characteristic of X-rays. At the same time it has been found that some of these phenomena undergo a gradual change as we proceed to the extreme frequencies of X-rays, and as a result of these interesting changes in the laws of optics we have gained new information regarding the nature of light.

It has not always been recognized that X-rays is a branch of optics. As a result of the early studies of Röntgen and his followers it was concluded that X-rays could not be reflected or refracted, that they were not polarized on transversing crystals, and that they showed no signs of diffraction on passing through narrow slits. In fact, about the only property which they were found to possess in common with light was that of propagation in straight lines. Many will recall also the heated debate between Barkla and Bragg, as late as 1910, one defending the idea that X-rays are waves like light, the other that they consist of streams of little bullets called « neutrons ». It is a debate on which the last word has not yet been said!

The refraction and reflection of X-rays

We should consider the phenomena of refraction and reflection as one problem, since it is a well-known law of optics that reflection can occur only from a boundary surface between two media of different indices of refraction. If *one* is found, the other *must* be present.

In his original examination of the properties of X-rays, Röntgen¹ tried unsuccessfully to obtain refraction by means of prisms of a variety of mate-

rials such as ebonite, aluminum, and water. Perhaps the experiment of this type most favorable for detecting refraction was one by Barkla². In this work X-rays of a wavelength which excited strongly the characteristic K-radiation from bromine were passed through a crystal of potassium bromide. The precision of his experiment was such that he was able to conclude that the refractive index for a wavelength of $0.5 \text{ \AA}$ probably differed from unity by less than five parts in a million.

Although these direct tests for refraction of X-rays were unsuccessful, Stenström observed³ that for X-rays whose wavelengths are greater than about $3 \text{ \AA}$, reflected from crystals of sugar and gypsum, Bragg's law, $n\lambda = 2D \sin \vartheta$, does not give accurately the angles of reflection. He interpreted the difference as due to an appreciable refraction of the X-rays as they enter the crystal. Measurements by Duane and Siegbahn and their collaborators⁴ showed that discrepancies of the same type occur, though they are very small indeed, when ordinary X-rays are reflected from calcite.

The direction of the deviations in Stenström's experiments indicated that the index of refraction of the crystals employed was less than unity. If this is the case also, for other substances, total reflection should occur when X-rays in air strike a polished surface at a sufficiently sharp glancing angle, just as light in a glass prism is totally reflected from a surface between the glass and air if the light strikes the surface at a sufficiently sharp angle. From a measurement of this critical angle for total reflection it should be possible to determine the index of refraction of the X-rays.

When the experiment was tried⁵ the results were strictly in accord with these predictions. The apparatus was set up as shown in Fig. 1, reflecting a

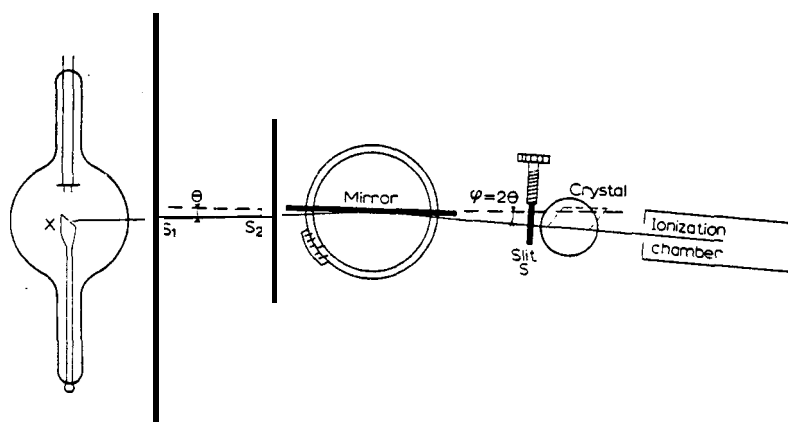


Fig. 1. Apparatus for studying the total reflection of X-rays.

narrow sheet of X-rays from a polished mirror on the crystal of a Bragg spectrometer. It was found that the beam could be reflected from the surfaces of a polished glass and silver through several minutes of arc. By studying the spectrum of the reflected beam, the critical glancing angle was found to be approximately proportional to the wavelength. For ordinary X-rays whose wavelength is one half an ångström, the critical glancing angle from crown glass was found to be about 4.5 minutes of arc, which means a reflective index differing from unity by less than one part in a million.

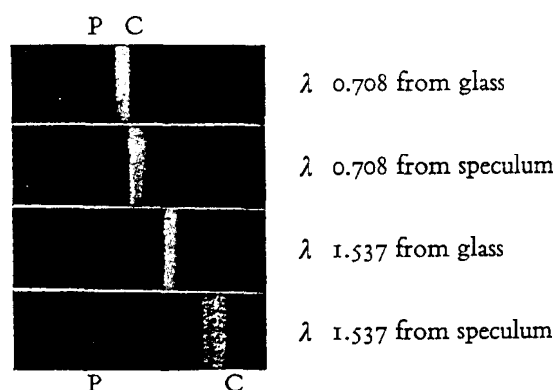


Fig. 2. Total reflection of X-rays from polished glass and speculum metal (Doan).
P = direct beam; C = critical angle of the totally reflected beam.

Fig. 2 shows some photographs of the totally reflected beam and the critical angle for total reflection taken recently from Dr. Doan⁶ working at Chicago. From the sharpness of the critical angle shown in this figure, it is evident that a precise determination of the refractive index can thus be made.

You will recall that when one measures the index of refraction of a beam of light in a glass prism it is customary to set the prism at the angle for minimum deviation. This is done primarily because it simplifies the calculation of the refractive index from measured angles. It is an interesting comment on the psychology of habit that most of the earlier investigators of the refraction X-rays by prisms also used their prisms set at the minimum deviation. Of course, since the *effect* to be measured was very small indeed, the adjustments should have been made to secure not the minimum deviation but the maximum possible. After almost thirty years of attempts to refract X-rays by prisms, experiments under the conditions to secure maximum re-

fraction were first performed by Larsson, Siegbahn, and Waller⁷, using the arrangement shown diagrammatically in Fig. 3. The X-rays struck the face of the prism at a fine glancing angle, just greater than the critical angle for the rays which are refracted. Thus the direct rays, the refracted rays, and the totally reflected rays of greater wavelength were all recorded on the same plate.

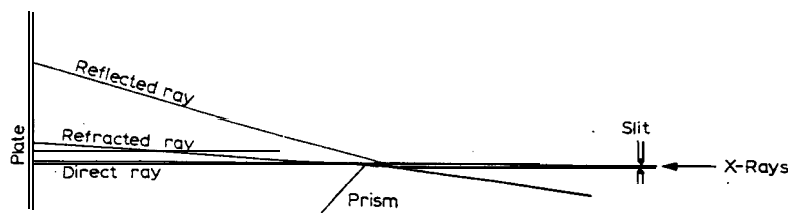


Fig. 3. Refraction of X-rays by a glass prism. (Arrangement of Larsson, Siegbahn, and Waller.)

Fig. 4 shows one of the resulting photographs. Here we see a complete dispersion spectrum of the refracted X-rays precisely similar to the spectrum obtained when the light is refracted by a prism of glass. The presence of the direct ray and the totally reflected ray on the same plate make possible all the angle measurements necessary for a precise determination of the refractive index of each spectrum line.

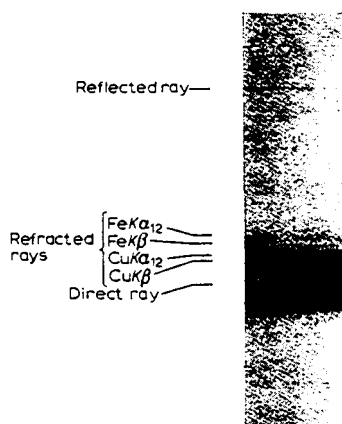


Fig. 4. Prism spectrum of X-rays obtained by Larsson, Siegbahn, and Waller.

For a generation we have been trying to obtain a quantitative test of Drude and Lorentz' dispersion theory in the ordinary optical region. But our ignorance regarding the number and the natural frequency of the electron oscillators in the refractive medium has foiled all such attempts. For the extreme frequencies of X-rays, however, the problem has become greatly simplified. In the case of substances such as glass, the X-ray frequencies are much higher than the natural frequencies of the oscillators in the medium, and the only knowledge which the theory requires is that of the number of electrons per unit volume in the dispersive medium. If we assume the number of electrons per atom to be equal to the atomic number, we are thus able to calculate at once the refractive index of the medium for X-rays. In the case of glass this calculation gives agreement with experiment within the experimental error, which is in some cases less than one per cent. So we may say that the laws of optical dispersion given by the electron theory are first established on a quantitative basis by these experiments on the refraction of X-rays.

Another way of looking at the problem is to assume the validity of the dispersion equation developed from the electron theory, and to use these measurements of refraction of X-rays to calculate the number of electrons in each atom of the refracting material. This affords us what is probably our most direct as well as our most precise means of determining this number. The precision of the experiments is now such that we can say that the number of electrons per atom effective in refracting X-rays is within less than one half of one per cent equal to the atomic number of the atom.

Thus optical refraction and reflection are extended to the region of X-rays, and this extension has brought with it more exact knowledge not only of the laws of optics but also of the structure of the atom.

The diffraction of X-rays

Early in the history of X-rays it was recognized that most of the properties of these rays might be explained if, as suggested by Wiechert⁸, they consist of electromagnetic waves much shorter than those of light. Haga and Wind performed a careful series of experiments⁹ to detect any possible diffraction by a wedge-shaped slit a few thousandths of an inch broad at its widest part. The magnitude of the broadening was about that which would result¹⁰ from rays of 1.3 Å wavelength. The experiments were repeated by yet more

refined methods by Walter and Pohl¹¹ who came to the conclusion that if any diffraction effects were present, they were considerably smaller than Haga and Wind had estimated. But on the basis of the photometric measurements of Walter and Pohl's plates by Koch¹² using his new photoelectric microphotometer, Sommerfeld found¹³ that their photographs indicated an effective wavelength for hard X-rays of 4 Å, and for soft X-rays a wavelength measurably greater.

It may have been because of their difficulty that these experiments did not carry as far as their accuracy would seem to have warranted. Nevertheless it was this work perhaps more than any other that encouraged Laue to undertake his remarkable experiments on the diffraction of X-rays by crystals.

Within the last few years Walter has repeated these slit diffraction experiments, making use of the $K\alpha$ -line of copper, and has obtained perfectly convincing diffraction effects¹⁴. Because of the difficulty in determining the width of the slit where the diffraction occurs, it was possible to make from his photographs only a rough estimate of the wavelength of X-rays. But within this rather large probable error the wavelength agreed with that determined by crystal spectrometry.

While these slit diffraction experiments were being developed, and long before they were brought to a successful conclusion, Laue and his collaborators discovered the remarkable fact that crystals act as suitable gratings for diffracting X-rays. You are all acquainted with the history of this discovery. The identity in nature of X-rays and light could no longer be doubted. It gave a tool which enabled the Braggs to determine with a definiteness previously almost unthinkable, the manner in which crystals are constructed of their elementary components. By its help, Moseley and Siegbahn have studied the spectra of X-rays, we have learned to count one by one the electrons in the different atoms, and we have found out something regarding the arrangement of these electrons. The measurement of X-ray wavelengths thus made possible gave Duane the means of making his precise determination of Planck's radiation constant. By showing the change of wavelength when X-rays are scattered, it has helped us to find the quanta of momentum of radiation which had previously been only vaguely suspected. Thus in the two great fields of modern physical inquiry, the structure of matter and the nature of radiation, the discovery of the diffraction of X-rays by crystals has opened the gateway to many new and fruitful paths of investigation. As Duc de Broglie has remarked, << if the value of a discovery is to be measured by fruitfulness of its consequences, the work of Laue and his collaborators

should be considered as perhaps the most important in modern physics)).

These are some of the consequences of extending the optical phenomenon of diffraction into the realm of X-rays.

There is, however, another aspect of the extension of optical diffraction into the X-ray region, which has also led to interesting results. It is the use of ruled diffraction gratings for studies of spectra. By a series of brilliant investigations, Schumann, Lyman, and Millikan, using vacuum spectrographs, have pushed the optical spectra by successive stages far into the ultraviolet. Using a concave reflection grating at nearly normal incidence, Millikan and his collaborators¹⁵ found a line probably belonging to the L-series of aluminum, of a wavelength as short as $136.6 \text{ \AA}$, only a twenty-fifth that of yellow light. Why his spectra stopped here, whether because of failure of his gratings to reflect shorter wavelengths, or because of lack of sensitiveness of the plates, or because his hot sparks gave no rays of shorter wavelength, was hard to say.

Röntgen had tried to get X-ray spectra by reflection from a ruled grating, but the task seemed hopeless, How could one get spectra from a reflection grating if the reflection grating would not reflect? But when it was found that X-rays could be totally reflected by fine glancing angles, hope for the success of such an experiment was revived. Carrara¹⁶, working at Pisa, tried one of Rowland's optical gratings, but without success. Fortunately we at

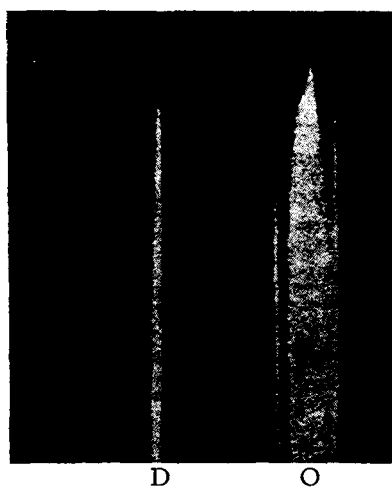


Fig. 5. Spectrum of the $K\alpha_1$ -line of molybdenum, $\lambda = 0.708 \text{ \AA}$, from a grating ruled on speculum metal (Compton and Doan). *D* marks the direct beam, and *O* the directly reflected beam.

Chicago did not know of this failure, and with one of Michelson's gratings ruled specially for this purpose, Doan found that he could get diffraction spectra of the K-series radiations both from copper and molybdenum¹⁷. Fig. 5 shows one of our diffraction spectra, giving several orders of the $K\alpha_1$ -line of molybdenum, obtained by reflection at a small glancing angle. This work was quickly followed by Thibaud¹⁸, who photographed a beautiful spectrum of the K-series lines of copper from a grating of only a few hundred lines ruled on glass. That X-ray spectra could be obtained from the same type of ruled reflection gratings as those used with light was now established.

The race to complete the spectrum between the extreme ultraviolet of Millikan and the soft X-ray spectra of Siegbahn began again with renewed enthusiasm. It had seemed that the work of Millikan and his co-workers had carried the ultraviolet spectra to as short wavelengths as it was possible to go. On the X-ray side, the long wavelength limit was placed, theoretically at least, by the spacing of the reflecting layers in the crystal used as a natural grating. De Broghe, W. H. Bragg, Siegbahn, and their collaborators were finding suitable crystals of greater and greater spacing until Thoriaeus and Siegbahn¹⁹, using crystals of palmitic acid, measured the La-line of chromium with a wavelength 21.69 Å. But there still remained a gap of almost three octaves between these X-rays and the shortest ultraviolet in which, though radiation had been detected by photoelectric methods, no spectral measurements has been made.

Thibaud, working in de Broglie's laboratory at Paris, made a determined effort to extend the limit of the ultraviolet spectrum, using his glass grating at glancing incidence²⁰. His spectra however stopped at 144 Å, a little greater than the shortest wavelength observed in Millikan's experiments.

But meanwhile, Dauvillier, also working with de Broglie, was making rapid strides working from the soft X-ray side of the gap. First²¹ using a grating of palmitic acid, he found the $K\alpha$ -line of carbon of wavelength 45 Å. Then²² using for a grating a crystal of the lead salt of melissic acid, with the remarkable grating space of 87.5 Å, he measured a spectrum line of thorium as long as 121 Å, leaving only a small fraction of an octave between his longest X-ray spectrum lines and Millikan's shortest ultraviolet lines. The credit for filling in the greater part of the remaining gap must thus be given to Dauvillier.

The final bridge between the X-ray and the ultraviolet spectra has however been laid by Osgood²³, a young Scotchman working with me at Chicago. He also used soft X-rays as did Dauvillier, but instead of a crystal

grating, he did his experiments with a concave glass grating in a Rowland mounting, but with the rays at glancing incidence. Fig. 6 shows a series of Osgood's spectra. The shortest wavelength here shown is the $K\alpha$ -line of carbon, 45 Å, and we see a series of lines up to 211 Å. An interesting feature of the spectra is an emission band in the aluminum spectrum at about 170 Å, which is probably in some way associated with the L-series spectrum of aluminum. These spectra overlap, on the short wavelength side, Dauvillier's crystal measurements, and on the other side of the great wavelengths, Millikan's ultraviolet spectra.

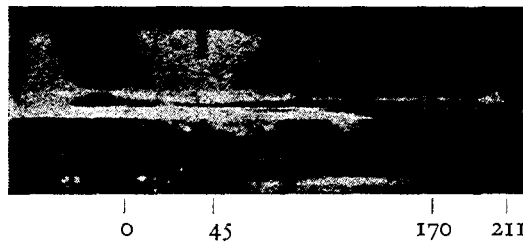


Fig. 6. Osgood's grating spectra of soft X-rays from Al, C, Mg, Fe, and Ni, showing lines from $\lambda = 45$ Å to $\lambda = 211$ Å. These are the first spectra bridging the gap between soft X-rays and the ultraviolet.

In the September number of *The Physical Review*, Hunt²⁴ describes similar experiments, using however a plane ruled grating at glancing incidence, in which he has measured lines from 2 Å down to the carbon line at 45 Å, thus meeting the shortest of Osgood's measurements. On the other hand, Fig. 7 shows some beautiful spectra of the extreme ultraviolet obtained recently by Dr. Hoag, working with Professor Gale at Chicago, using a concave grating at grazing incidence. These spectra extend from 200 Å to 1760 Å, overlapping Osgood's X-ray spectra on the short wavelength side and reaching the ordinary ultraviolet region on the side of the great wavelengths. Thus from the extreme infrared to the region of the ordinary X-rays we now have a continuous series of spectra from ruled gratings.

Whatever we may find regarding the nature of X-rays, it would take a bold man indeed to suggest, in light of these experiments, that they differ in nature from ordinary light.

It is too early to predict what may be the consequences of these grating measurements of X-rays. It seems clear, however, that they must lead to a new and more precise knowledge of the absolute wavelength of crystals.

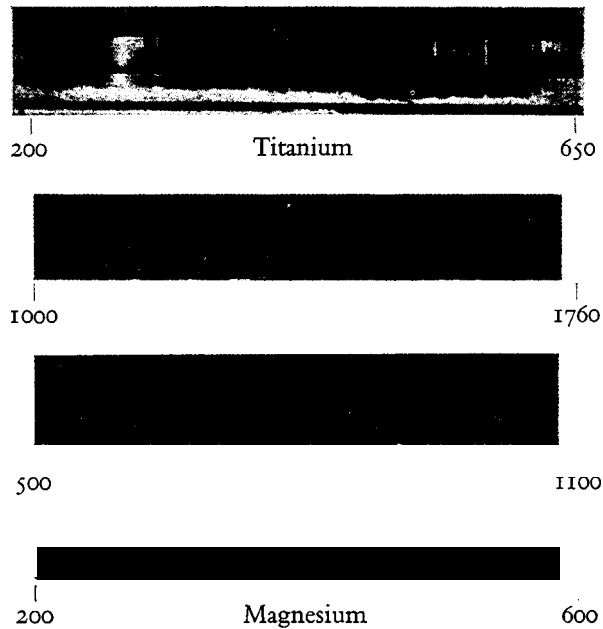


Fig. 7. Spectra of the extreme ultraviolet, from Mg and Ti, 200 Å to 1760 Å (Hoag).

This will in turn afford a new means of determining Avogadro's number and the electronic charge, which should be of precision comparable with that of Millikan's oil drops.

The scattering of X-rays and light

The phenomena that we have been considering are ones in which the laws which have been found to hold in the optical region apply equally well in the X-ray region. This is not the case, however, for all optical phenomena.

The theory of the diffuse scattering of light by turbid media has been examined by Drude, Lord Rayleigh, Raman, and others, and an essentially similar theory of the diffuse scattering of X-rays has been developed by Thomson, Debye, and others. Two important consequences of these theories are, (1) that the scattered radiation shall be of the same wavelength as the primary rays; and (2) that the rays scattered at 90 degrees with the primary rays shall be plane polarized. The experimental tests of these two predictions have led to interesting results.

A series of experiments performed during the last few years* has shown that secondary X-rays are of greater wavelength than the primary rays which produce them. This work is too well-known to require description. On the other hand, careful experiments to find a similar increase in wavelength in light diffusely scattered by a turbid medium have failed to show any effect^{2,5}. An examination of the spectrum of the secondary X-rays shows that the primary beam has been split into two parts, as shown in Fig. 8, one of the same wavelength and the other of increased wavelength. When

* For an account of this work, see e.g. the writer's *X-rays and Electrons*, Chap. g, Van Nostrand, 1926.

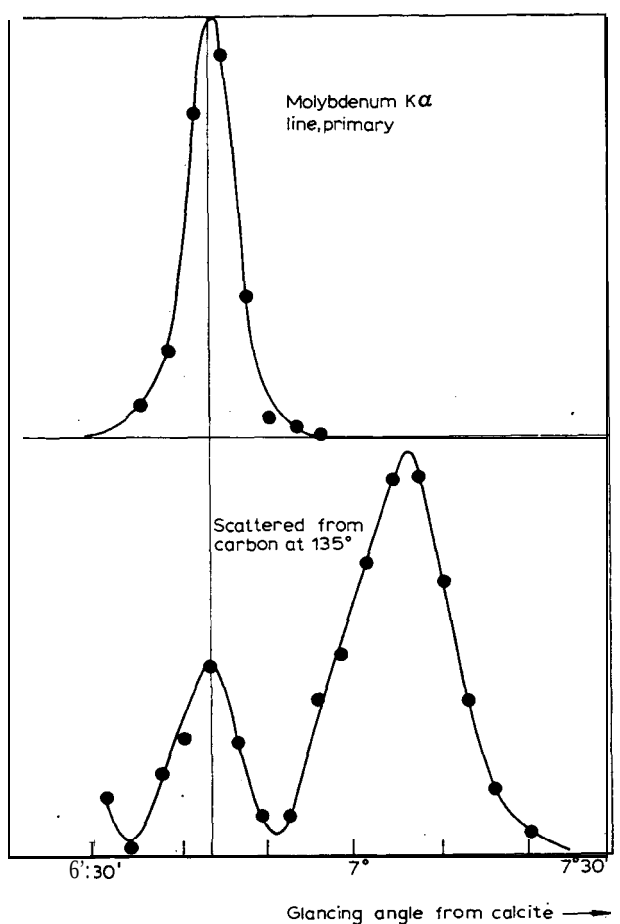


Fig. 8. A typical spectrum of scattered X-rays, showing the splitting of the primary ray into a modified and an unmodified ray.

different primary wavelengths are used, we find always the same difference in wavelength between these two components; but the relative intensity of the two components changes. For the longer wavelengths the unmodified ray has the greater energy, while for the shorter wavelengths the modified ray is predominant. In fact when hard y-rays are employed, it is not possible to find any radiation of the original wavelength.

Thus in the wavelength of secondary radiation we have a gradually increasing departure from the classical electron theory of scattering as we go from the optical region to the region of X-rays and y-rays.

The question arises, are these secondary X-rays of increased wavelength to be classed as scattered X-rays or as fluorescent? An important fact bearing on this point is the intensity of the secondary rays. From the theories of Thomson, Debye, and others it is possible to calculate the absolute intensity of the scattered rays. It is found that this calculated intensity agrees very nearly with the total intensity of the modified and unmodified rays, but that in many cases the observed intensity of the unmodified ray taken alone is very small compared with the calculated intensity. If the electron theory of the intensity of scattering is even approximately correct, we must thus include the modified with the unmodified rays as scattered rays.

Information regarding the origin of these secondary rays is also given by their state of polarization. We have called attention to the fact that the electron theory demands that the X-rays scattered at 90 degrees should be completely plane polarized. If the rays of increased wavelength are fluorescent, however, we should not expect them to be strongly polarized. You will remember the experiments performed by Barkla²⁶ some twenty years ago in which he observed strong polarization in X-rays scattered at right angles. It was this experiment which gave us our first strong evidence of the similar character of X-rays and light. But in this work the polarization was far from complete. In fact the intensity of the secondary rays at 90 degrees dropped only to one third its maximum value, where as for complete polarization it should have fallen to zero.

The fact that no such unpolarized rays exist was established by repeating Barkla's experiment²⁷ with scattering blocks of different sizes. When very small blocks were used, we found that the polarization was nearly complete. The lack of complete polarization in Barkla's experiments was due chiefly to the multiple scattering of the X-rays in the large blocks that he used to scatter the X-rays. It would seem that the only explanation of the complete polarization of the secondary rays is that they consist wholly of scattered rays.

According to the classical theory, an electromagnetic wave is scattered when it sets the electrons which it traverses into forced oscillations, and these oscillating electrons reradiate the energy which they receive. In order to account for the change in wavelength of the scattered rays, however, we have had to adopt a wholly different picture of the scattering process, as shown in Fig. g. Here we do not think of the X-rays as waves but as light corpuscles, quanta, or, as we may call them, photons. Moreover, there is nothing here of the forced oscillation pictured on the classical view, but a sort of elastic collision, in which the energy and momentum are conserved.

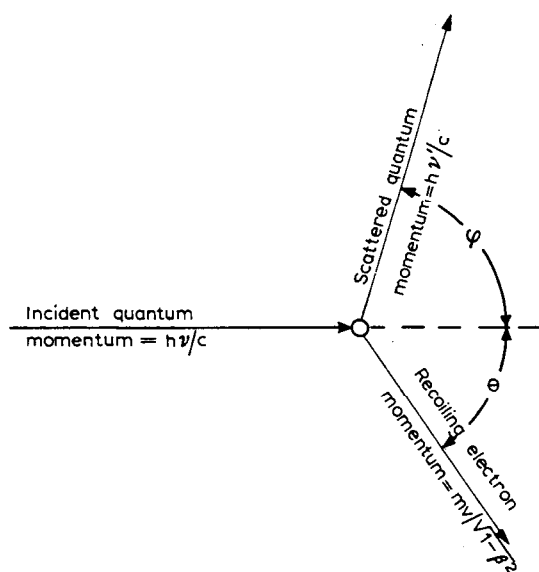


Fig. 9. An X-ray photon is deflected through an angle ϕ by an electron, which in turn recoils at an angle θ , taking a part of the energy of the photon.

This new picture of the scattering process leads at once to three consequences that can be tested by experiment. There is a change of wavelength

$$\delta\lambda = \frac{h}{mc} (1 - \cos \phi) \quad (1)$$

which accounts for the modified line in the spectra of scattered X-rays. Experiment has shown that this formula is correct within the precision of our

knowledge of h , m , and c . The electron which recoils from the scattered X-rays should have the kinetic energy

$$E_{kin} = h\nu \cdot \frac{h\nu}{mc^2} \cos^2\theta \quad (2)$$

approximately. When this theory was first proposed, no electrons of this type were known; but they were discovered by Wilson²⁸ and Bothe²⁹ within a few months after their prediction. Now we know that the number, energy, and spatial distribution of these recoil electrons are in accord with the predictions of the photon theory. Finally, whenever a photon is deflected at an angle ϕ , the electron should recoil at an angle q given by the relation

$$\cot \frac{1}{2}\phi = \tan \theta \quad (3)$$

approximately.

This relation we have tested³⁰, using the apparatus shown diagrammatically in Fig. 10. A narrow beam of X-rays enters a Wilson expansion

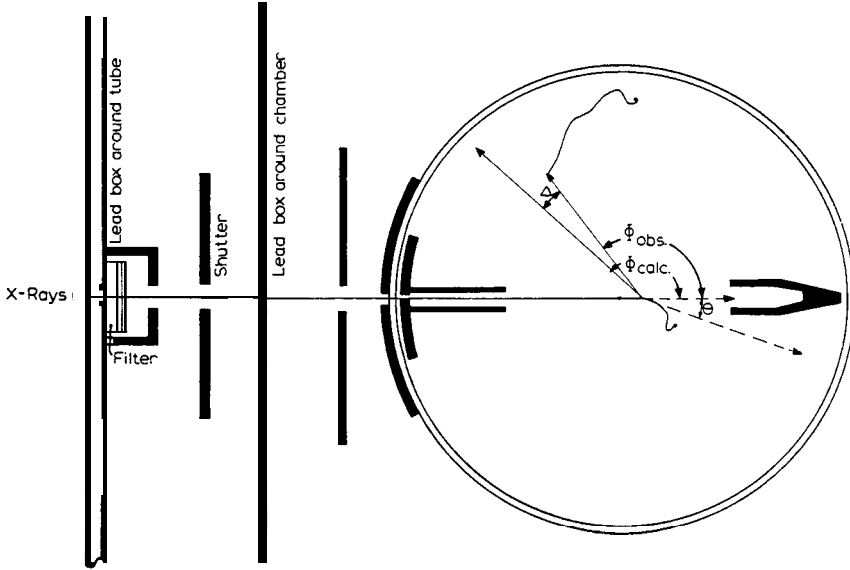


Fig. 10. An electron recoiling at an angle q should be associated with a photon deflected through an angle j .

chamber. Here it produces a recoil electron. If the photon theory is correct, associated with this recoil electron, a photon is scattered in the direction j . If it should happen to eject a b -ray, the origin of this b -ray tells the direction in which the photon was scattered. Fig. 11 shows a typical photograph of the process. A measurement of the angle θ at which the recoil electron on this plate is ejected and the angle j of the origin of the secondary P-particle, shows close agreement with the photon formula. This experiment is of especial significance, since it shows that for each recoil electron there is a scattered photon, and that the energy and momentum of the system photon plus electron are conserved in the scattering process.

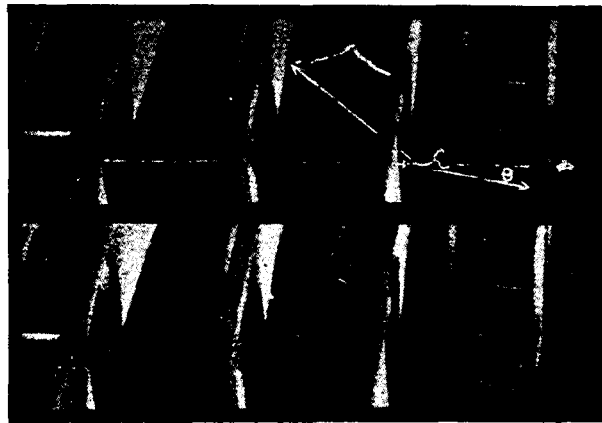


Fig. 11. Photograph showing recoil electron and associated secondary b -ray. (The upper photograph is retouched.)

The evidence for the existence of directed quanta of radiation afforded by this experiment is very direct. The experiment shows that associated with each recoil electron there is scattered X-ray energy enough to produce a secondary b -ray, and that this energy proceeds in a direction determined at the moment of ejection of the recoil electron. Unless the experiment is subject to improbably large experimental errors, therefore, the scattered X-rays proceed in the form of photons.

Thus we see that as a study of the scattering of radiation is extended into the very high frequencies of X-rays, the manner of scattering changes. For the lower frequencies the phenomena could be accounted for in terms of waves. For these higher frequencies we can find no interpretation of the scattering except in terms of the deflection of corpuscles or photons of radia-

tion. Yet it is certain that the two types of radiation, light and X-rays, are essentially the same kind of thing. We are thus confronted with the dilemma of having before us a convincing evidence that radiation consists of waves, and at the same time that it consists of corpuscles.

It would seem that this dilemma is being solved by the new wave mechanics. De Broglie³¹ has assumed that associated with every particle of matter in motion there is a wave whose wavelength is given by the relation

$$mv = h/\lambda$$

where mv is the momentum of the particle. A very similar assumption was made at about the same time by Duane³², to account for the diffraction of X-ray photons. As applied to the motion of electrons, Schrödinger has shown the great power of this conception in studying atomic structure³³. It now seems, through the efforts of Heisenberg, Bohr, and others, that this conception of the relation between corpuscles and waves is capable of giving us a unified view of the diffraction and interference of light, and at the same time of its diffuse scattering and the photoelectric effect. It would however take too long to describe these new developments in detail.

We have thus seen how the essentially optical properties of radiation have been recognized and studied in the realm of X-rays. A study of the refraction and specular reflection of X-rays has given an important confirmation of the electron theory of dispersion, and has enabled us to count with high precision the number of electrons in the atom. The diffraction of X-rays by crystals has given wonderfully exact information regarding the structure of crystals, and has greatly extended our knowledge of spectra. When X-rays were diffracted by ruled gratings, it made possible the study of the complete spectrum from the longest to the shortest waves. In the diffuse scattering of radiation, we have found a gradual change from the scattering of waves to the scattering of corpuscles.

Thus by a study of X-rays as a branch of optics we have found in X-rays all of the well-known wave characteristics of light, but we have found also that we must consider these rays as moving in directed quanta. It is these changes in the laws of optics when extended to the realm of X-rays that have been in large measure responsible for the recent revision of our ideas regarding the nature of the atom and of radiation.

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Biography

Arthur Holly Compton was born at Wooster, Ohio, on September 10th, 1892, the son of Elias Compton, Professor of Philosophy and Dean of the College of Wooster. He was educated at the College, graduating Bachelor of Science in 1913, and he spent three years in postgraduate study at Princeton University receiving his M.A. degree in 1914 and his Ph.D. in 1916. After spending a year as instructor of physics at the University of Minnesota, he took a position as a research engineer with the Westinghouse Lamp Company at Pittsburgh until 1919 when he studied at Cambridge University as a National Research Council Fellow. In 1920, he was appointed Wayman Crow Professor of Physics, and Head of the Department of Physics at the Washington University, St. Louis; and in 1923 he moved to the University of Chicago as Professor of Physics. Compton returned to St. Louis as Chancellor in 1945 and from 1954 until his retirement in 1961 he was Distinguished Service Professor of Natural Philosophy at the Washington University.

In his early days at Princeton, Compton devised an elegant method for demonstrating the Earth's rotation, but he was soon to begin his studies in the field of X-rays. He developed a theory of the intensity of X-ray reflection from crystals as a means of studying the arrangement of electrons and atoms, and in 1918 he started a study of X-ray scattering. This led, in 1922, to his discovery of the increase of wavelength of X-rays due to scattering of the incident radiation by free electrons, which implies that the scattered quanta have less energy than the quanta of the original beam. This effect, nowadays known as the Compton effect, which clearly illustrates the particle concept of electromagnetic radiation, was afterwards substantiated by C. T. R. Wilson who, in his cloud chamber, could show the presence of the tracks of the recoil electrons. Another proof of the reality of this phenomenon was supplied by the coincidence method (developed by Compton and A.W. Simon, and independently in Germany by W. Bothe and H. Geiger), by which it could be established that individual scattered X-ray photons and recoil electrons appear at the same instant, contradicting the views then being developed by some investigators in an attempt to reconcile quantum views with

the continuous waves of electromagnetic theory. For this discovery, Compton was awarded the Nobel Prize in Physics for 1927 (sharing this with C. T. R. Wilson who received the Prize for his discovery of the cloud chamber method).

In addition, Compton discovered (with C. F. Hagenow) the phenomenon of total reflection of X-rays and their complete polarization, which led to a more accurate determination of the number of electrons in an atom. He was also the first (with R. L. Doan) who obtained X-ray spectra from ruled gratings, which offers a direct method of measuring the wavelength of X-rays. By comparing these spectra with those obtained when using a crystal, the absolute value of the grating space of the crystal can be determined. The Avogadro number found by combining above value with the measured crystal density, led to a new value for the electronic charge. This outcome necessitated the revision of the Millikan oil-drop value from 4.774 to 4.803×10^{-10} e.s.u. (revealing that systematic errors had been made in the measurement of the viscosity of air, a quantity entering into the oil-drop method).

During 1930-1940, Compton led a world-wide study of the geographic variations of the intensity of cosmic rays, thereby fully confirming the observations made in 1927 by J. Clay from Amsterdam of the influence of latitude on cosmic ray intensity. He could, however, show that the intensity was correlated with geomagnetic rather than geographic latitude. This gave rise to extensive studies of the interaction of the Earth's magnetic field with the incoming isotropic stream of primary charged particles.

Compton has numerous papers on scientific record and he is the author of *Secondary Radiations Produced by X-rays* (1922), *X-Rays and Electrons* (1926, second edition 1928), *X-Rays in Theory and Experiment* (with S. K. Allison, 1935, this being the revised edition of *X-rays and Electrons*), *The Freedom of Man* (1935, third edition 1939), *On Going to College* (with others, 1940), and *Human Meaning of Science* (1940).

Dr. Compton was awarded numerous honorary degrees and other distinctions including the Rumford Gold Medal (American Academy of Arts and Sciences), 1927; Gold Medal of Radiological Society of North America, 1928; Hughes Medal (Royal Society) and Franklin Medal (Franklin Institute), 1940.

He served as President of the American Physical Society (1934), of the American Association of Scientific Workers (1939-1940), and of the American Association for the Advancement of Science (1942).

In 1941 Compton was appointed Chairman of the National Academy of Sciences Committee to Evaluate Use of Atomic Energy in War. His investigations, carried out in cooperation with E. Fermi, L. Szilard, E. P. Wigner and others, led to the establishment of the first controlled uranium fission reactors, and, ultimately, to the large plutonium-producing reactors in Hanford, Washington, which produced the plutonium for the Nagasaki bomb, in August 1945. (He also played a role in the Government's decision to use the bomb ; a personal account of these matters may be found in his book, *Atomic Quest-a Personal Narrative*, 1956.)

In 1916, he married Betty Charity McCloskey. The eldest of their two sons, Arthur Allen, is in the American Foreign Service and the youngest, John Joseph, is Professor of Philosophy at the Vanderbilt University (Nashville, Tennessee). His brother Wilson is a former President of the Washington State University, and his brother Karl Taylor was formerly President of the Massachusetts Institute of Technology.

Compton's chief recreations were tennis, astronomy, photography and music.

He died on March 15th, 1962, in Berkeley, California.

CHARLES T. R. WILSON

On the cloud method of making visible ions and the tracks of ionizing particles

Nobel Lecture, December 12, 1927

In September 1894 I spent a few weeks in the Observatory which then existed on the summit of Ben Nevis, the highest of the Scottish hills. The wonderful optical phenomena shown when the sun shone on the clouds surrounding the hill-top, and especially the coloured rings surrounding the sun (coronas) or surrounding the shadow cast by the hill-top or observer on mist or cloud (glories), greatly excited my interest and made me wish to imitate them in the laboratory.

At the beginning of 1895 I made some experiments for this purpose - making clouds by expansion of moist air after the manner of Coulier and Aitken. Almost immediately I came across something which promised to be of more interest than the optical phenomena which I had intended to study. Moist air which had been freed from Aitken's dust particles, so that no cloud was formed even when a considerable degree of supersaturation was produced by expansion, did appear to give a cloud if the expansion and consequent supersaturation exceeded a certain limit. A quantitative expansion apparatus (Fig. 1) was therefore made in which given samples of moist air could repeatedly be allowed to expand suddenly without danger of contamination, and in which the increase of volume to be made could be adjusted at will.

It was found that there was a definite critical value for the expansion ratio ($v_2/v_1 = 1.25$) corresponding to an approximately fourfold supersaturation. In moist air which had been freed from Aitken's nuclei by repeatedly forming a cloud and allowing the drops to settle, no drops were formed unless the expansion exceeded this limit, while if it were exceeded, a shower of drops was seen to fall. The number of drops in the shower showed no diminution however often the process of producing the shower and allowing the drops to fall was repeated. It was evident then that the nuclei were always being regenerated in the air. A note describing these experiments was read before the Cambridge Philosophical Society in May 1895.

Further experiments with somewhat more elaborate apparatus (Fig. 2)

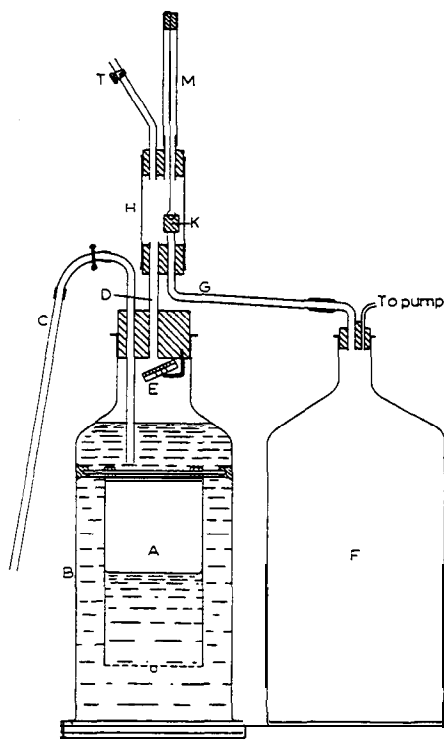


Fig. 1.

which allowed of more sudden expansion showed that there was a second critical expansion corresponding to an approximately eightfold supersaturation of the vapour. With expansions exceeding this limit, dense clouds were formed in dust-free air, the number of drops in the cloud increasing with very great rapidity as the expansion was increased beyond it and giving rise on account of their small and uniform size to very beautiful colour phenomena. The number of drops for expansions between the two limits remained small - the resulting condensation resembling a shower of rain rather than a cloud. The results were not essentially different in the various pure gases tried - although the expansion required to produce a given supersaturation was naturally different.

While the obvious explanation of the dense clouds formed when the second supersaturation limit was exceeded was that here we had condensation occurring in the absence of any nuclei other than the molecules of the vapour or gas - those responsible for the rain-like condensation which occurred when the supersaturation lay between the two limits from the first, excited

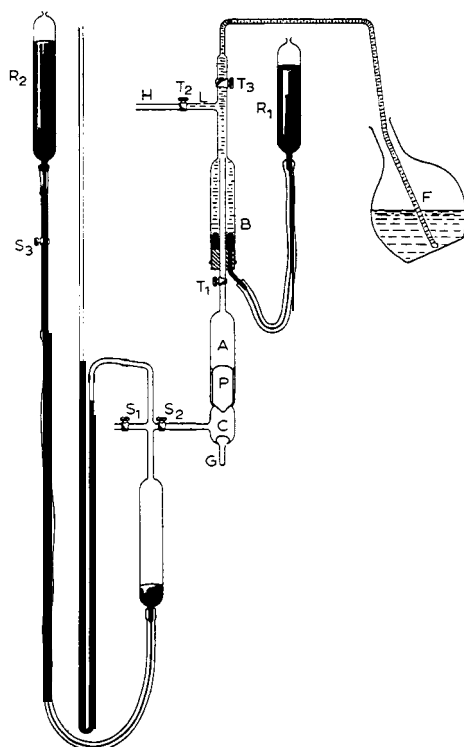


Fig.2.

my interest. The very fact that their number was so limited and yet that they were always being regenerated, together with the fact that the supersaturation required indicated a magnitude not greatly exceeding molecular dimensions, at once suggested that we had a means of making visible and counting certain individual molecules or atoms which were at the moment in some exceptional condition. Could they be electrically charged atoms or ions?*

In the autumn of 1895 came the news of Röntgen's great discovery. At the beginning of 1896 J. J. Thomson was investigating the conductivity of air exposed to the new rays - and I had the opportunity of using an X-ray tube of the primitive form then used which had been made by Prof. Thomson's assistant Mr. Everett in the Cavendish Laboratory. I can well recall my delight when I found at the first trial that while no drops were formed on expansion of the cloud chamber when exposed to X-rays if the expansion were less than 1.25, a fog which took many minutes to fall was produced

* The striking effect of point discharges on condensation in a steam jet had been attributed to ions by H. v. Helmholtz and Richarz.

when the expansion lay between the rain-like and cloud-like limits; X-rays thus produced in large numbers nuclei of the same kind as were always being produced in very small numbers in the air within the cloud chamber.

A short note describing this experiment was communicated to the Royal Society in March 1896.* The full paper containing the detailed account of the measurement of the two cloud limits in different gases was communicated a year later.

During the following two years I investigated by means of the expansion apparatus the condensation nuclei produced in gases by X-rays, by the newly discovered uranium rays, by ultraviolet light, by point discharges and other agents.

The purely ionizing agents all produced nuclei, identical as regards the minimum supersaturation required to cause water to condense upon them.

The condensation nuclei produced by these ionizing agents were shown to be indeed themselves the ions by their behaviour in an electric field. They could be completely removed by applying an electric field before expansion - so that no cloud was formed.

Uncharged nuclei, not removable by a field, were also found to be produced in various ways and their properties were investigated.

A paper describing these investigations was communicated to the Royal Society in the autumn of 1898.

The following winter was occupied in studying separately the phenomena of condensation on positive and negative ions. It was found that the measurement of the least expansion required to condense water in ionized air or other gas had all been concerned with the negative ion; to catch the positive ion the expansion ratio v_2/v_1 , had to exceed a limit of about 1.31, corresponding to an approximately sixfold supersaturation instead of the fourfold supersaturation required by the negative ion.

This paper marked the completion of a stage in my work, the behaviour of ions as condensation nuclei. It was now possible to make visible the individual ions and to distinguish between positive and negative ions.

This found its immediate application in the determination of the charge carried by an ion by Thomson and later by H. A. Wilson. The method used by the latter of partially balancing the weight of a charged drop by a known electric field and determining the change in the rate of fall did not however

* Richarz about the same time described the action of X-rays on condensation in the steam jet.

really depend essentially on the charge being due to condensation on an ion; and Millikan, whose earlier experiments were made by H. A. Wilson's method, soon abandoned the use of water drops and the expansion method.

It is, I think, of some interest that the value of the elementary charge e , deduced directly from the degree of supersaturation required to cause negative ions to grow into visible drops, is 4.9×10^{-10} e.s.u.; it agrees within 1 per cent with Millikan's accurately determined value.

My own researches at this time were directed in another direction. Since the nuclei responsible for the rain-like condensation in air not exposed to known ionizing agents require just the same degree of supersaturation to make water condense upon them as do the ions produced by X-rays and other ionizing agents, it seemed almost certain that they also are ions. Experiments were therefore made to find if there was a measurable conduction of electricity through air in a closed vessel containing dust-free air. These led at once to positive results, and proved that the air in a closed vessel is always ionized. Quite independently and approaching the matter from a different side, Geitel was working at the subject in Germany and arrived at the same conclusion; his paper was published very shortly before mine. My own experiments were performed on a small scale, the method used being one afterwards very largely employed, in which the rate of loss of charge was measured from an insulated system consisting of a short metal rod with a gold leaf attached which was suspended in an ionization chamber in such a way that the possibility of leakage along the supports was eliminated.

These experiments were carried out in 1900, and they led me naturally to further experiments on conduction in closed vessels, to the direction of radioactive matter carried down by rain and snow, to the direct measurement of the current between the atmosphere and the earth, and to the study of atmospheric electricity generally.

With the exception of some experiments published in 1904 proving directly that the nuclei causing the ordinary rain-like condensation are removable by an electric field and are therefore ions (an experiment which required for success a somewhat larger expansion apparatus than that which had been used in the condensation experiments on the ions produced by X-rays) my experimental work on condensation phenomena was not resumed for many years.

Among the experimental work on the subject carried out by others in this period, in addition to the determination of the electronic charge, that on condensation phenomena in other vapours than water by Przibram and by

Laby should be mentioned. These investigations showed that water vapour is quite exceptional in condensing more readily on the negative than on the positive ion; a connection between the relative efficiency of the positive and negative ions and the sign of the electrical charges developed on splashing - the Lenard effect - was established.

Towards 1910 I began to make experiments with a view to increasing the usefulness of the condensation method.

I had from the time of my first experiments on condensation of water vapour on the ions had in view the possibility of determining the ionic charge by a direct method, in which the ions carrying a known charge were to be made visible by condensation, photographed and counted. The plan which I had in view on resuming the work was that of measuring an intermittent current from a negatively charged plate exposed to ultraviolet light within the cloud chamber, thus obtaining a stream of ions divided into groups, and finding the number of ions per group by the condensation method.

Again in the years which had elapsed since my earlier experiments, ideas on the corpuscular nature of α - and β -rays had become much more definite, and I had in view the possibility that the track of an ionizing particle might be made visible and photographed by condensing water on the ions which it liberated. As I succeeded in this latter aim, and Millikan had by this time rendered the other project unnecessary, the determination of $\langle e \rangle$, by the method of direct counting of drops was never carried out.

Much time was spent in making tests of the most suitable form of expansion apparatus and in finding an efficient means of instantaneous illumination of the cloud particles for the purpose of photographing them. In the spring of 1911 tests were still incomplete, but it occurred to me one day to try whether some indication of the tracks might not be made visible with the rough apparatus already constructed. The first test was made with X-rays, with little expectation of success, and in making an expansion of the proper magnitude for condensation on the ions while the air was exposed to the rays I was delighted to see the cloud chamber filled with little wisps and threads of clouds - the tracks of the electrons ejected by the action of the rays. The radium-tipped metal tongue of a spintharoscope was then placed inside the cloud chamber and the very beautiful sight of the clouds condensed along the tracks of the α -particles was seen for the first time. The long thread-like tracks of fast β -particles were also seen when a suitable source was brought near the cloud chamber.

Some rough photographs were obtained and were included in a short communication to the Royal Society made in April 1911.

The summer of 1911 was occupied in designing improved apparatus. The expansion apparatus (Fig. 3) was constructed in the workshop of the Cavendish Laboratory and is the one which I have had in use up to the present time. In the winter which followed, the photographs were obtained which formed the basis of a paper communicated to the Royal Society in the following June (1912).

The essential conditions to be fulfilled if good pictures of the tracks are to be obtained are mainly these. The expansion must be effected without stirring up the gas; this condition is secured by using a wide, shallow cloud chamber of which the floor can be made to drop suddenly and so produce the desired increase of volume. The cloud chamber must be freed not only from <<dust>> particles, but from ions other than those produced by the ionizing particles under observation; an electric field maintained between the roof and floor of the cloud chamber serves this purpose.

For the purpose of obtaining sharp pictures of the tracks, the order of operations has to be : firstly, the production of the necessary supersaturation by sudden expansion of the gas; secondly, the passage of the ionizing par-

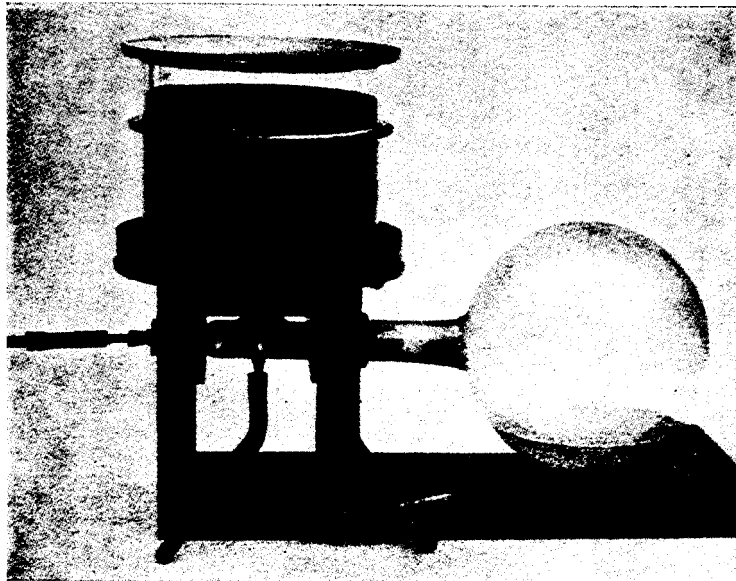


Fig.3.

titles through the supersaturated gas; and finally, the illumination of the cloud condensed on the ions along the track.

Perhaps the most important purpose that the photographs obtained at this time served, was to confirm, in a way which was free from ambiguity, conclusions which had already been reached by less direct means and which in some cases, but not in all, had come to be generally accepted.

I remember showing W. H. Bragg one of the first good pictures of α -ray tracks very shortly after it was obtained. He at once showed me a diagram which he had just published showing examples of what he considered likely forms for the paths of α -rays. The similarity between the actual photograph and Bragg's ideal picture was astonishing. (Lantern slides from photographs of α -particle cloud-tracks taken at this time were shown - Figs. 4 and 5.)



Fig. 4.



Fig. 5.

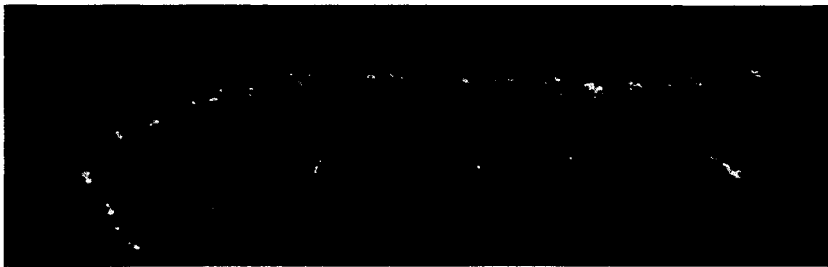


Fig. 6.

The tracks of electrons were of remarkable straightness when the velocity was high, but slower electrons (Fig. 6) showed both sudden deflections

through large angles and gradual deviations due to an accumulation of small deflections - Rutherford's single and compound scattering. Both types of scattering were also shown in the last part of the course of the α -particles.

The pictures of the clouds condensed in air exposed to a beam of X-rays showed perfectly clearly that the primary effect of the rays is to eject electrons with considerable velocity from atoms in the path of the beam, and that the ionization is due to the action of these secondary β -particles. This was in accordance with the conclusions at which W. H. Bragg had arrived.

Information as to the nature of the ionization by β -particles was afforded by the photographs (e.g. Fig. 6). As was stated in the paper published in 1912, the ions along the track of a β -particle occur partly in pairs, partly in groups; and the groups were interpreted as indicating that in certain cases an electron ejected from an atom by a β -particle may itself have energy enough to ionize. This result appeared to be overlooked in later discussions as to the nature of ionization by β -particles.

Further photographs were taken in the winter of 1912-1913, especially illustrating the effects of X-rays. Some of these were exhibited at lectures before the Royal Institution and the French Physical Society, and published in their journals. Among these were pictures showing the effects of placing a sheet of metal, e.g. silver (Fig. 7), in the path of a beam of X-rays. These showed very clearly the absorption by the screen of the primary radiation; and the absorption by the air of the characteristic radiations from a copper or silver screen was also shown by the clouds condensed along tracks of the electrons which they ejected.

The tracks of the electrons ejected from a thin copper screen as a result of the absorption of the primary X-rays was also well shown (Fig. 8) ; the excess of the number ejected on the side of emergence being conspicuous. In obtaining the pictures which best showed this effect, the intensity of the radiation was reduced by introducing a plate of aluminium about 1 cm in thickness which removed especially the less penetrating rays. A very interesting feature appears in these photographs. It is described in the concluding paragraph of the *Journal de Physique* paper:

<<A great number of the rays emitted by the copper and the air under the influence of the X-rays are extraordinarily long; some attain a length which in air at atmospheric pressure corresponds to nearly three centimetres. It should be added, however, that on the path of the primary X-rays one can see a large number of little patches of cloud, which perhaps represent the

paths of exceedingly short cathode rays, and of which the interpretation requires further investigation.>>

These very short tracks, we now know, are due to the Compton effect; they are the tracks of recoiling electrons, each of which has scattered a quantum of radiation.

At this stage of the work, some stereoscopic pictures of cloud tracks were obtained; and the advantages of such virtually three-dimensional pictures were so apparent that henceforth this method was exclusively used. A number of stereoscopic pictures of α -ray tracks and of the tracks of electrons ejected by X-rays had been obtained when war broke out.

Work on the tracks was entirely laid aside during the war. When it was resumed (at the Solar Physics Observatory, to which I was now attached) it was some time before good pictures were obtained, not till the autumn of

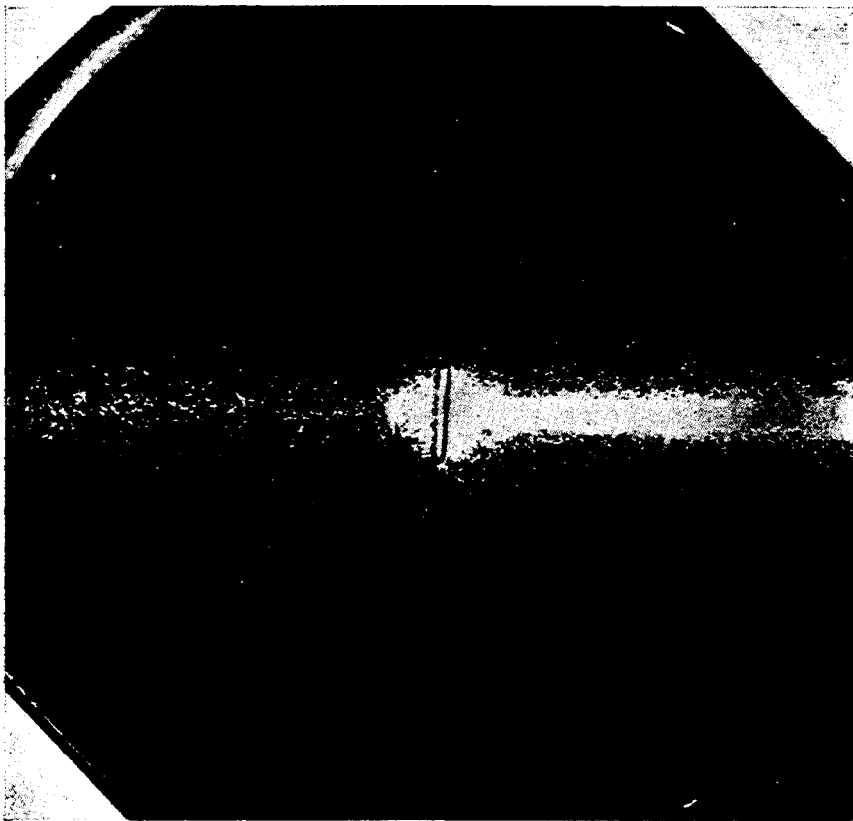


Fig. 7.

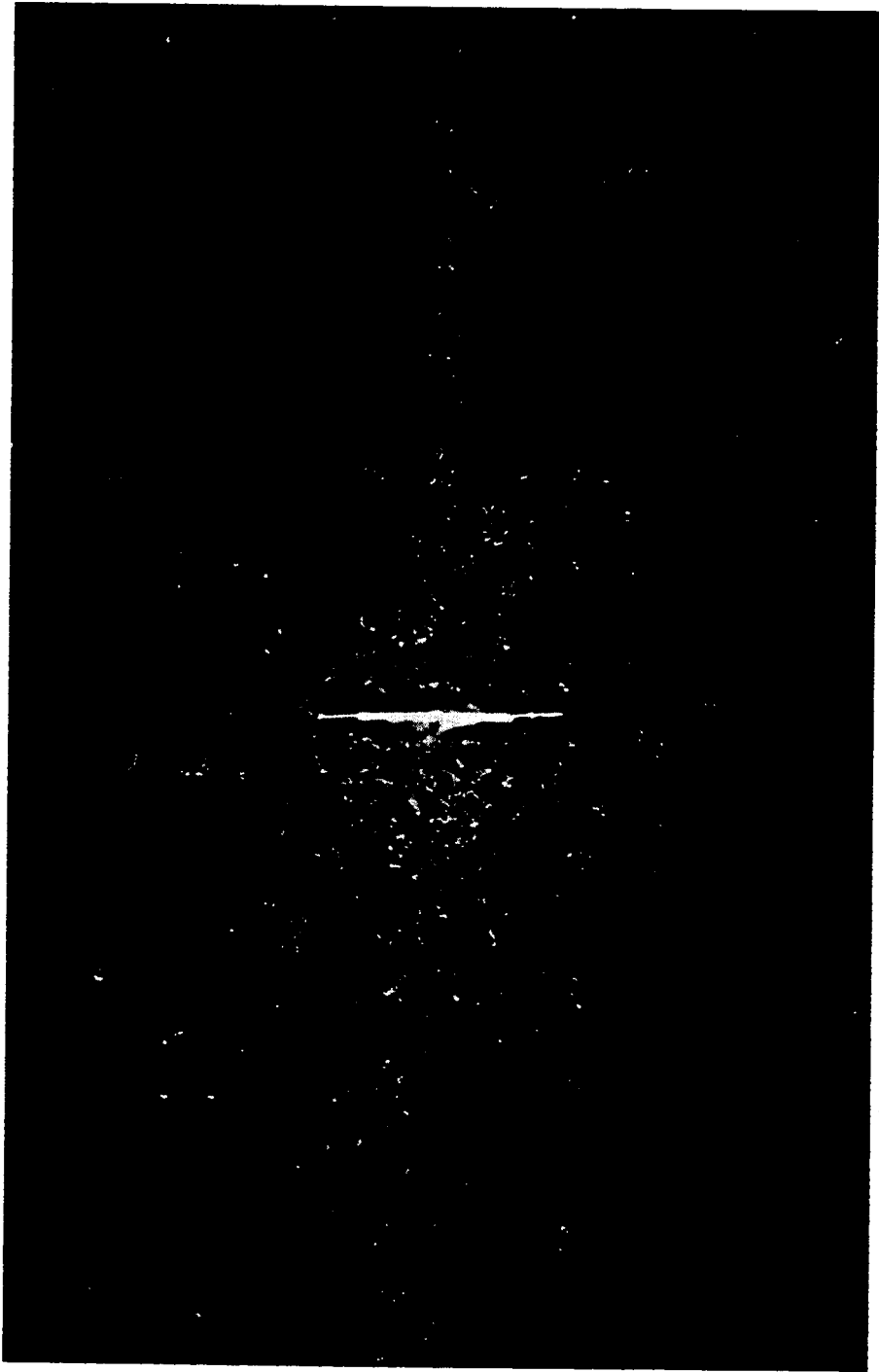


Fig. 8.

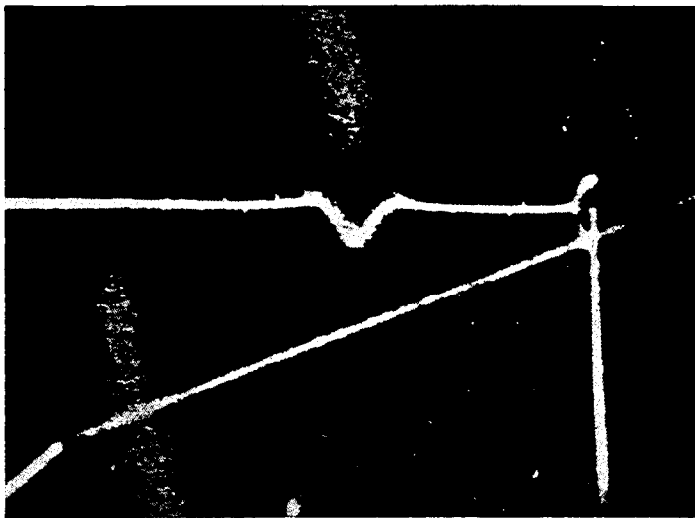


Fig. 9.

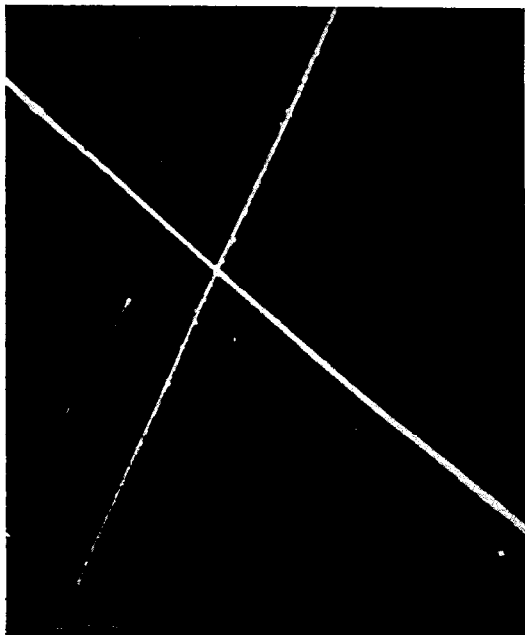


Fig. 10.

1921. A number of stereoscopic pictures of α -ray tracks were then obtained with some thorium emanation in the cloud chamber; some of these pictures were of interest and were published in November 1922. They showed well, for example (Figs.9 and 10), the separation by an electric field of the positive and negative ions liberated along the track of an α -particle which traversed the cloud chamber before expansion; the two associated tracks of α -particles from an atom of thorium emanation and from the resulting thorium A atom; the track of the recoiling atom which has ejected an α -particle; and the tracks of δ -rays (electrons ejected by the α -particle with velocity comparable with its own) projecting from the initial portions of α -ray tracks. The tracks of δ -rays due to α -rays in hydrogen had been photographed some years before by Bumstead in America.



Fig. II.

The experiments on the effects of X-rays and of the electrons ejected by them, which had been interrupted by the war, were now resumed, and a number of stereoscopic pictures were obtained between December 1921 and July 1922. These contained a large amount of material for study and the results were not ready for publication till June 1923. When the cloud chamber is momentarily traversed by a beam of X-rays of suitable intensity a picture (Fig. II) is obtained (in three dimensions if the stereoscopic method is used) of the tracks of all the electrons ejected from a given volume of the gas by the action of the X-rays, primary and secondary. An examination of the picture shows at once : (1) the point of origin of each β -ray (electron track); (2) its initial direction (i.e. the direction in which an electron has been ejected from its parent atom by the action of the radiation) ; (3) its range or total length of its path; (4) the form of the track, its sudden or gradual bends, and the number and direction of emission of any secondary β -rays (branches); and (5) the variation of ionization along the track; under favourable

conditions the number and distribution of the ions along the tracks may be obtained by direct counting.

The general results obtained can hardly be indicated otherwise than by showing examples of the photographs. Unfortunately I am not able to show them stereoscopically on the screen.

1. The first picture (Fig. 12) shows the absolutely straight track of a fast electron, and the devious tracks of electrons of which the energy corresponds to less than about 20,000 volts.
2. This (Fig. 13) shows the track of an electron of moderate energy: the straightness of the initial portion - a deviation through a large angle as a result of a close approach to the nucleus of an atom - the increasing curvature of the track and increasing ionization as the velocity diminishes.
3. Here (Fig. 14) the primary electron has ejected from an atom a secondary electron with energy enough to form a conspicuous branch track.
4. This (Fig. 15) is the track of a very fast electron passing through air at rather low pressure. In this picture the drops condensed on positive and negative ions are individually visible, and occur sometimes in pairs, sometimes in groups. The electron ejected from an atom by the primary p-particle has in many cases emerged with insufficient energy to produce further ionization; in other cases the energy of the ejected electron has been sufficient to produce one or more additional pairs of ions by collision.
5. In a large number of cases (e.g. Fig. 16) while the individual ions could not be counted, it was easy to determine the number of groups, i.e. the primary ionization or number of atoms from which an electron was ejected per cm of path.
6. This (Fig. 17) shows the tracks of electrons ejected by the K-radiations from silver.
7. The next picture (Fig. 18) shows the tracks of those ejected under identical conditions by the K-rays from copper.

From data such as those contained in these two pictures it was possible to measure the ranges of electrons of known initial energy. The range in air was found to be 1 cm for an electron of about 21,000 volts, and to vary according to Whiddington's law of the fourth power of the velocity. This result was utilized in determining the primary ionization for electrons of approximately known velocity.

8. The next picture (Fig. 19) was obtained by passing a very narrow beam of hard X-rays through a thin copper plate. Only two tracks appeared in the photograph, that of an electron ejected from the copper by the primary

beam, and a short one, in the air outside the primary beam, of range corresponding to ejection of an electron by copper K-radiation. We almost certainly have here the tracks of the copper K-electron whose ejection was followed by the emission of a quantum of copper K-radiation, and of the electron ejected from nitrogen or oxygen as a result of the absorption of this same quantum of copper K-radiation.

9. A quite similar picture (Fig. 20) obtained with a narrow beam of hard X-rays passing through a platinum plate.

10. Similarly related tracks may occur, both of which have their origin in the air. This picture (Fig. 21) shows the most common case (one independently discovered by Auger and explained, and very thoroughly investigated by him). Here both tracks start from the same atom; the K-radiation (or the energy which might have been spent in emitting it) being used in ejecting an outer electron from the atom from which the X-rays had ejected a K-electron.

The remaining pictures (Figs. 22, 23, and 24) show the cloud tracks obtained when horizontal beams of X-rays traversed the cloud chamber from right to left. They show, as some of the pictures obtained in 1913 had already indicated, that two classes of *b*-rays are produced by such rays, giving << long >> tracks and << short >> tracks.

A << long >> track is the track of a photoelectron, i.e. of an electron ejected as the result of absorption of a quantum of X-radiation. The number of short tracks was found to be very small relatively to that of the long tracks when the wavelength of the incident radiation is as great as one ångström. It increases rapidly as the wavelength diminishes, and for short wavelengths the number greatly exceeds that for the long tracks. At the same time the short tracks which are mere << sphere tracks >> when they are due to the longer waves become << fish tracks >>; they begin to have a measurable range, and their appearance shows that they are due to electrons ejected nearly along the direction of propagation of the primary beam.

It was pointed out in the 1923 paper that the phenomena relating to these tracks supported A. H. Compton's theory of the scattering of X-rays, and that they are in all probability just the tracks of the recoiling electrons which according to this theory have scattered individual quanta of radiation.

It was pointed out by Compton that the relative numbers of the short and long tracks for a given wavelength of the incident radiation in these photographs are in agreement with the ratio between the scattering and absorption coefficients, and that this in itself furnishes strong support for his theory.

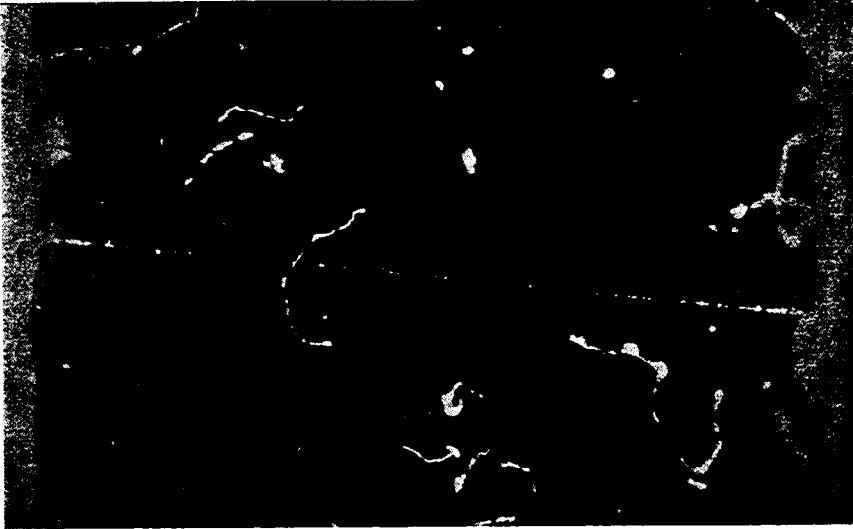


Fig. 12.



Fig. 13.

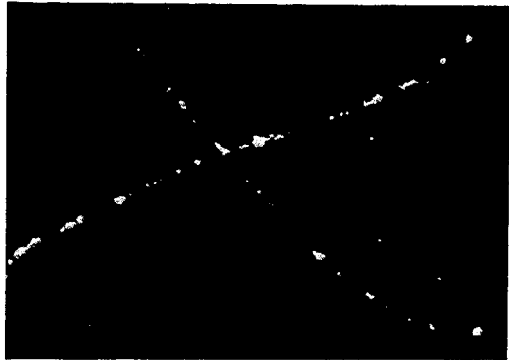


Fig. 16.

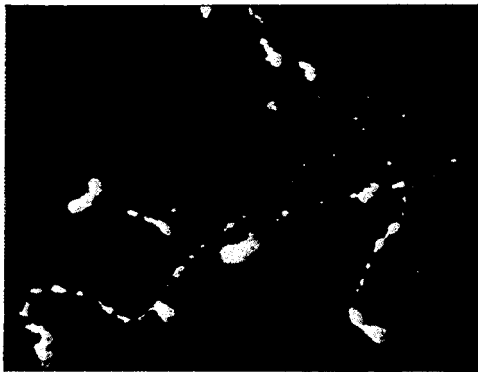


Fig. 14.

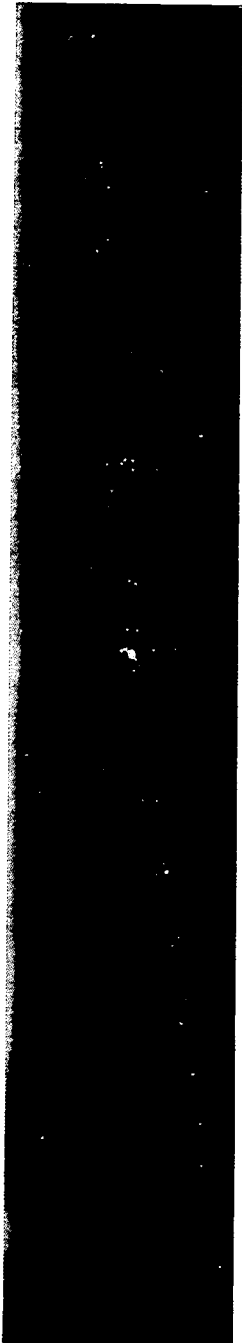


Fig. 15.



Fig. 18.



Fig. 17.

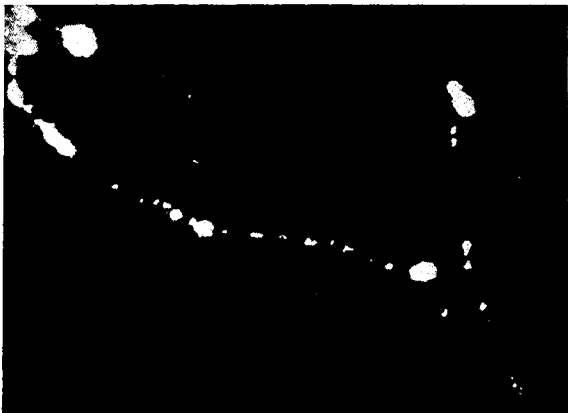


Fig. 21

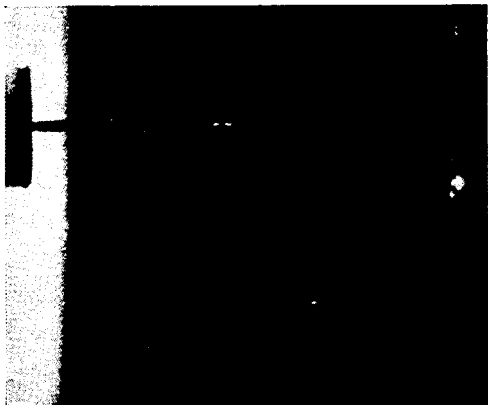


Fig. 20.

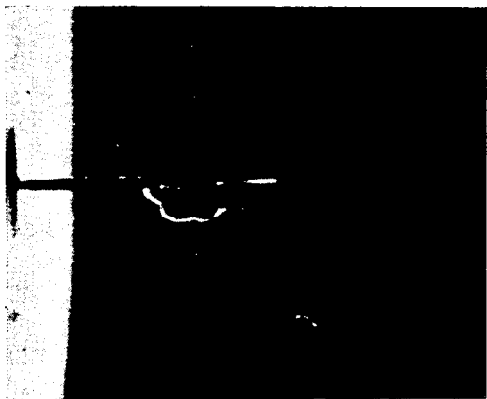


Fig. 19.

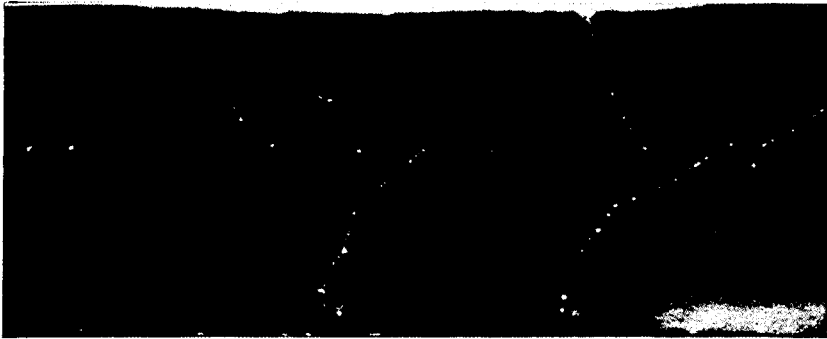


Fig. 22.

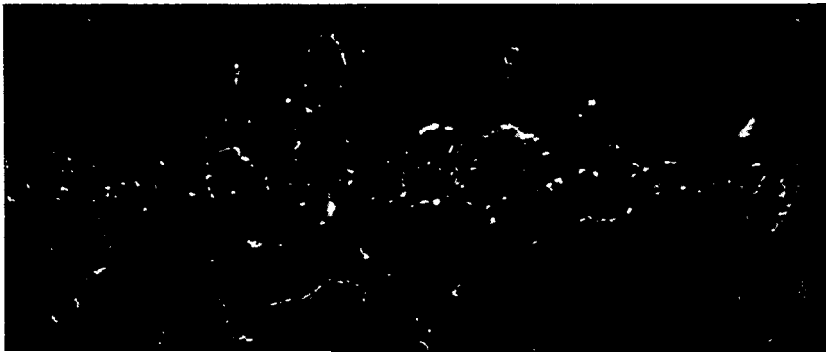


Fig. 23.



Fig. 24.

Nuttall and Williams have later investigated the relative numbers of long and short tracks in cloud photographs with homogeneous X-rays of different wavelengths in pure gases. This investigation as well as other recent cloud experiments, such as those of Compton and his collaborators, afford strong confirmation of Compton's theory and leave no room for doubt that the <<fish tracks>> are the tracks of the recoil electrons of that theory; each represents the scattering of a quantum of radiation.

The long tracks, i.e. the tracks of electrons ejected as a result of absorption of a quantum of radiation may be initially nearly at right angles to the beam of X-rays or may be inclined at considerable angles to this direction. In my own observations the number which had a forward component in their velocity was found considerably to exceed those with a backward component; and the ratio of the number with a forward to the number with a backward component increased with increasing frequency of the radiation. Qualitatively at least one may explain this result by saying that the momentum of the absorbed quantum is given to the ejected electron. The matter has been investigated much more fully by Auger and others.

I have tried to give some account of the history of the development of the cloud method.

During the last few years many physicists have been using the method; in some cases with refinements which made it possible to attain an accuracy much exceeding that arrived at in my experiments. It would take too long even to enumerate these investigations. But I should like to mention as examples of the applications of the method: the work of Blackett on collisions of α -particles with atomic nuclei and on atomic disintegrations thus produced, on the ranges of individual α -particles by Mlle Curie and by Miss Meitner, on δ -rays by Chadwick and Emeleus, on the mobility of radioactive ions by Dee, on X-rays and the β -rays associated with them by Bothe, by Auger, by Nuttall and Williams, and by Compton and his collaborators; and on the study of the wavelengths of γ -radiations, by measurement of the ranges of the Compton recoil electrons, by Skobelzyn.

Biography

Charles Thomson Rees Wilson was born on the 14th of February, 1869, in the parish of Glencorse, near Edinburgh. His father, John Wilson, was a farmer, and his ancestors had been farmers in the South of Scotland for generations. His mother was Annie Clerk Harper.

At the age of four he lost his father, and his mother moved with the family to Manchester, where he was at first educated at a private school, and later at Owen's College-now the University of Manchester. Here, intending to become a physician, Wilson took up mainly biology. Having been granted an entrance scholarship in 1888 he went on to Cambridge (Sidney Sussex College), where he took his degree in 1892. It was here that he became interested in the physical sciences, especially physics and chemistry. (It was also possible that Wilson's decision to abandon medicine was influenced by Balfour Stewart, who was professor of physics at Owen's College at that time-about a dozen years earlier, J. J. Thomson, who also went to Cambridge, had passed through the same College.)

When standing on the summit of Ben Nevis, the highest of the Scottish mountains, in the late summer of 1894, Wilson was struck by the beauty of coronas and <<glories>> (coloured rings surrounding shadows cast on mist and cloud), and he decided to imitate these natural phenomena in the laboratory (early 1895). His sharp observation and keen intellect, however, led him to suspect (after a few months' work at the Cavendish Laboratory) that the few drops reappearing again and again each time he expanded a volume of moist, dust-free air, might be the result of condensation on nuclei-possibly the ions causing the <<residual>> conductivity of the atmosphere-produced continuously. Wilson's hypothesis was supported after exposure (early 1896) of his primitive *cloud chamber* to the newly discovered (end of 1895) X-rays. The immense increase of the <<ram-like>> condensation fitted excellently with the observation made by Thomson and McClelland, immediately after Röntgen's discovery, that air was made conductive by the passage of X-rays. When, during the summer of that year, it was firmly established by Thomson and Rutherford that the conductivity was indeed due to ionization of

the gas, there was no longer any doubt that ions in gases could be detected and, photographically, recorded and thus studied at leisure. Wilson's appointment as Clerk Maxwell Student, at the end of that year, enabled him to devote all his time for the next three years to research, and for a year subsequent to this he was employed by the Meteorological Council in research on atmospheric electricity. The greater part of his work on the behaviour of ions as condensation nuclei was thus carried out in the years 1905-1909, whilst after this his other occupations-mainly tutorial-prevented him from dealing sufficiently with the development of the cloud chamber. Early in 1911, however, he was the first person to see and photograph the tracks of individual α - and β -particles and electrons. (The latter were described by him as <<little wisps and threads of clouds>>.) The event aroused great interest as the paths of the α -particles were just as W. H. Bragg had drawn them in a publication some years earlier. But it was not until 1923 that the cloud chamber was brought to perfection and led to his two, beautifully illustrated, classic papers on the tracks of electrons. Wilson's technique was promptly followed with startling success in all parts of the world-in Cambridge, by Blackett (who in 1948 received the Nobel Prize on account of his further development of the cloud chamber and his discoveries made therewith) and Kapitza; in Paris, by Irène Curie and Auger; in Berlin, by Bothe, Meitner, and Philipp; in Leningrad, by Skobelzyn; in Tokio, by Kikuchi.

Some of the most important achievements using the Wilson chamber were: the demonstration of the existence of Compton recoil electrons, thus establishing beyond any doubt the reality of the Compton effect (Compton shared the Nobel Prize with Wilson in 1927); the discovery of the positron by Anderson (who was awarded the Nobel Prize for 1936 for this feat); the visual demonstration of the processes of <<pair creation>> and <<annihilation>> of electrons and positrons by Blackett and Occhialini; and that of the transmutation of atomic nuclei carried out by Cockcroft and Walton. Thus, Rutherford's remark that the cloud chamber was <<the most original and wonderful instrument in scientific history>> has been fully justified.

In 1900 Wilson was made Fellow of Sidney Sussex College, and University Lecturer and Demonstrator. From then until 1918 he was in charge of the advanced teaching of practical physics at the Cavendish Laboratory, and also gave lectures on light. As well as his experimental work at the Cavendish Laboratory, he also made observations (1900-1901) on atmospheric electricity (mainly in the surroundings of Peebles in Scotland). In 1913, he

was appointed Observer in Meteorological Physics at the Solar Physics Observatory, and most of his research both on the tracks of ionizing particles and on thunderstorm electricity was carried out there. In 1918, he was appointed Reader in Electrical Meteorology, and in 1925, Jacksonian Professor of Natural Philosophy. He was elected a Fellow of the Royal Society in 1900, and this Society also honoured him with the Hughes Medal (1911), a Royal Medal (1922), and the Copley Medal (1935). The Cambridge Philosophical Society awarded him the Hopkins Prize (1920), and the Royal Society of Edinburgh the Gunning Prize (1921), while the Franklin Institute presented him the Howard Potts Medal (1925).

After his retirement Wilson moved to Edinburgh, and later, at the age of 80, to the village of Carlops, close to his birthplace at the farmhouse of Crosshouse, at Glencorse. Life after this, however, was not an empty one: C.T.R. as his friends and colleagues called him, maintained social contacts, making a weekly journey by bus to the city to lunch with them. Scientifically, too, he was active to the end, finishing his long-promised manuscript on the theory of thundercloud electricity (*Proc. Roy. Soc. London*, August (1956)).

Among the few who enjoyed his personal guidance may be mentioned: Wormell (in the general field of atmospheric electricity), C. F. Powel (Nobel Prize winner 1950, for his development of the photographic method of studying nuclear processes and the discoveries made therewith on mesons), P. I. Dee and J. G. Wilson.

In 1908, Professor Wilson married Jessie Fraser, daughter of Rev. G. H. Dick of Glasgow; there were two sons and two daughters.

He died on the 15th of November, 1959, in the midst of his family.