W ILLIAM L AWRENCE B RAGG

The diffraction of X-rays by crystals

Nobel Lecture, September 6, 1922*

It is with the very greatest pleasure that I take this opportunity of expressing my gratitude to you for the great honour which you bestowed upon me, when you awarded my father and myself the Nobel Prize for Physics in the year 1915. In other years scientists have come here to express their thanks to you, who have received this great distinction for the work of an illustrious career devoted to research. That you should have given me, at the very out-set of my scientific career, even the most humble place amongst their ranks, is an honour of which I cannot but be very proud.

You invited me here two years ago, after the end of the war, but a series of unfortunate circumstances made it impossible for me to accept your invi-tation. I have always profoundly regretted this, and it was therefore with the very greatest satisfaction that I received the invitation of Prof. Arrhenius a few months ago, and arranged for this visit. I am at last able to tell you how deeply grateful I am to you, and to give you my thanks in person.

You have already honoured with the Nobel Prize Prof. von Laue, to whom we owe the great discovery which has made possible all progress in a new realm of science, the study of the structure of matter by the diffraction of X-rays. Prof von Laue, in his Nobel Lecture, has described to you how he was led to make his epochal discovery. In trying to think of some way in which diffraction effects with X-rays might be found, and the question of their true nature answered, he came to the realization that Nature had pro-vided, in a crystal, a diffraction grating exactly suited for the purpose. It had already been surmised that the X-rays, if they were in truth electromagnetic waves, would be found to have a very short wavelength, of the order of 10^{-9} centimetre. The work of Sohnke, Fedorov, and others on the geometry of crystal structure had shown that the atoms or molecules in a crystal must be arranged in a geometrical pattern with perfect regularity, and it was possible to calculate that the spacing of the pattern must be of the order of 10^{-8}

centimetre. The relation between this spacing and the conjectured wavelength of the X-rays was precisely that required to give diffraction effects. Von Laue, in collaboration with Friedrich and Knipping, tried the experiment of passing a narrow beam of X-rays through a crystal, and they were immediately successful in obtaining undoubted evidence of regular diffraction. The lines of investigation which this discovery opened up have been so numerous and fruitful that Prof. von Laue could only give the briefest review of them in his address to you. When we consider the advances in our knowledge of the structure of matter which have been made by means of the von Laue effect, this discovery must surely be regarded as occupying a unique position in the history of science.

In saying something about the work for which we were awarded the Nobel Prize, I feel that I cannot but speak for both my father and myself. It was with his inspiration and under his guidance that any contributions of my own were made, and it was one of the proudest moments of my life when I heard that you had associated my name with his and awarded the prize to us jointly.

Prof. von Laue had made some of his earliest experiments with a crystal of zinc sulphide, and had obtained results which proved that the diffracted pencils showed the symmetry of the underlying crystal structure, which in this case was cubic. He developed a mathematical theory of diffraction by a space lattice, and proved that these diffracted pencils were in directions which were to be expected for a series of diffracting points arranged on a cubic space lattice. In pursuing the analysis still further, he tried to account for the fact that, whereas there were a large number of directions in which one would expect to find a diffracted beam, only a certain number of these appeared on the photographic plate used to record the effect. He suggested that this might be accounted for by the existence, in the X-ray beam, of certain wavelengths alone; and that a diffracted beam only appeared when conditions were right for diffracting these wavelengths. In studying his work, it occurred to me that perhaps we ought to look for the origin of this selection of certain directions of diffraction in the peculiarities of the crystal structure, and not in the constitution of the X-ray beam; this might be of the nature of white light and be composed of a continuous range of wavelengths. I tried to attack the problem from a slightly different point of view, and to see what would happen if a series of irregular pulses fell on diffracting points arranged on a regular space lattice. This led naturally to the consideration of the diffraction effects as a reflexion of the pulses by the planes of the crystal structure. The

points of a space lattice may be arranged in series of planes, parallel and equidistant from each other. As a pulse passes over each diffracting point, it scatters a wave, and if a number of points are arranged on a plane the diffracted wavelets will combine together to form a reflected wave front, according to the well-known Huygens construction.

The pulses reflected by successive planes build up a wave train, which analysis shows to be composed of the wavelengths given by the formula

$$n\lambda = 2d \sin \vartheta$$

In this expression, n is an integer, λ is the wavelength of the X-rays, d the spacing of the planes, and ϑ the glancing angle at which the X-rays are reflected.

To regard the diffraction as a reflexion of the X-rays involved no new principle that was not already contained in von Laue's mathematical treatment. It still left open the question why certain planes in the zinc blende structure appeared to reflect strongly, while others which were apparently equally well adapted to do so were not represented by diffracted pencils. In analysing von Laue's result, however, I found that the selection of the effective planes could be accounted for by assuming that the diffracting centres were arranged in a face-centred cubic lattice, and not on a simple cubic lattice. The structural unit of the face-centred cubic lattice is a cube with a point at each comer and at the centre of each face. When the planes of such a lattice are arranged in the order of those most densely packed with atoms, and so most effective for reflexion, this order is rather different to that for a simple cubic lattice. By assigning a face-centred cubic structure to zinc blende, it seemed possible to explain satisfactorily the von Laue photograph as due to the diffraction of white radiation with a maximum intensity in a certain part of the spectrum. I made a further test of two simple cubic crystals, sodium chloride and potassium chloride. While the von Laue photographs obtained with sodium chloride indicated a face-centred lattice, those obtained with potassium chloride were of a simpler nature, and were such as one would expect from an arrangement of points at the corners of cubes. Since it seemed probable that these two crystals had a similar structure, I was led to conjecture that the atoms were arranged as shown in Fig. 1, where every corner of the cube is occupied by an atom, whereas the atoms of one kind considered alone are arranged on a face-centred lattice. In potassium chloride the atoms are so nearly equal in their weight that they act as equivalent diffracting centres and the structure may be regarded as a simple cubic one.
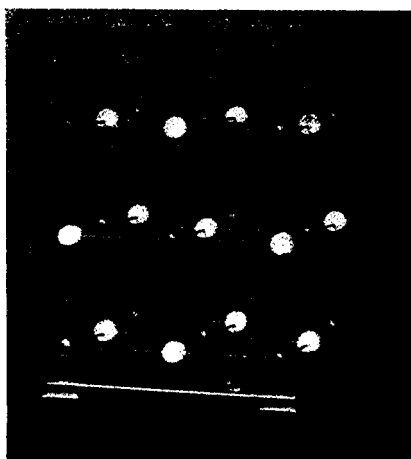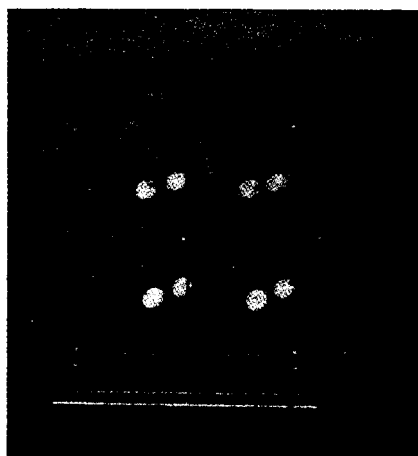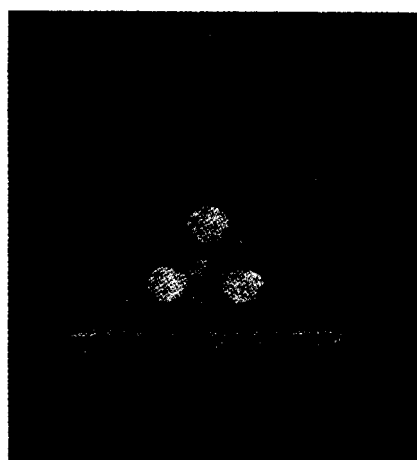
Fig. 1.

Fig. 2.

Fig. 3.

Fig. 1. *Rocksalt type (NaCl, KCl, LiF, etc.).* The *white balls* represent sodium (or chlorine); the *black balls,* chlorine (or sodium).

Fig. 2. *Fluorspar (CaF).* The *black balls* represent calcium; the *white balls,* fluorine.

Fig. 3. *Diamond.* Both *black* and *white balls* represent carbon atoms. Each ball is at the centre of gravity of four others.

Although it seemed certain that the von Laue effect was due to the diffraction of very short waves, there remained the possibility that there might not be the X-rays. My father, in order to test this, examined whether the beam reflected by a crystal ionized a gas; this he found to be the case. He examined the strength of the reflexion at various angles, and the instrument which was first used for the purpose was developed later into the X-ray spectrometer with which we have done the greater part of our work. In this instrument the X-rays coming from a tube are limited to a narrow beam by slits, and fall on a crystal at the centre of the spectrometer table by which they are

reflected; the reflected beam is received and measured in an ionization chamber.

In examining the effect for varying angles of incidence my father discovered that a very strong reflexion appeared when a given crystal face was set at certain definite angles. Since the relationship which has been mentioned above must hold between glancing angle and wavelength, this constituted the first evidence of the existence of characteristic "lines" in the radiation given off by the anticathode. These same lines could be recognized in the reflexions from other faces, and the measurement of the angles at which they appeared proved a most powerful method of finding the arrangement of the atoms in the crystal. The structures of sodium chloride and potassium chloride, which had been suggested by the von Laue photographs, were established on a firm basis by means of the spectrometer, and more complex struc-
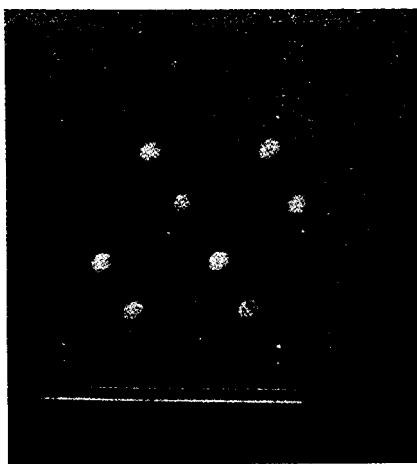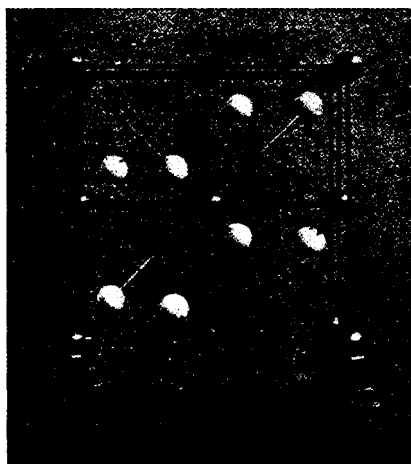

Fig. 4.   Fig. 5.

Fig. 4. *Iron pyrites (FeS₂)*. The arrangement may be considered as a modification of CaF_2. The *black balls* are the iron atoms. Each *white ball*, now representing a sulphur atom is displaced from the centre of the cube as in CaF_2 along a diagonal: the diagonal is chosen in a special way, best grasped from the model. A trigonal axis passes through the two white balls which lie close together and near the centre of the whole figure.

Fig. 5. *Iron pyrites*. Viewed from a different angle, which shows the disposition of the sulphur atoms in horizontal lines. These are parallel to the well-known markings on the FeS_2 crystal. If the viewpoint is altered, as by turning the model through a right angle about a vertical axis, or an axis in the plane of the paper, the disposition of the sulphur atoms appears vertical instead of horizontal: just as the marking do.
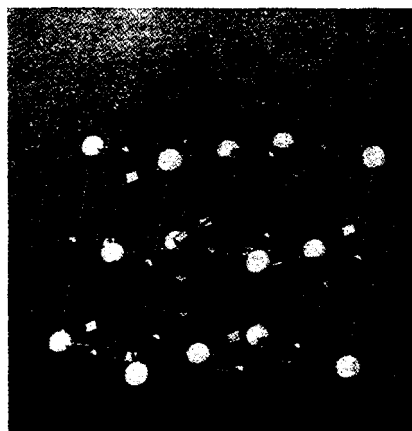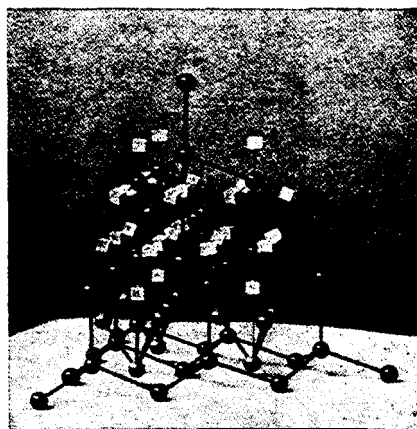
Fig. 6.

Fig. 7.

Fig. 6. *Calcite (CaCO₃)*. The *white balls* represent calcium; the *black balls,* carbon; and the *cubes,* oxygen.

Fig. 7. *Spinel structure (spinel MgAl₂O₄; magnetite FeFe₂O₄; gahnite ZnAl₂O₄; etc.).* The divalent atoms (Mg, Fe, Zn, etc.) are placed with respect to each other in the same way as the carbon atoms in a diamond and are represented by the *black balls.* The *grey balls* represent the trivalent atoms (Al, Fe, etc.) A grey ball lies at the centre of every hexagonal (benzene) ring of black balls. The *light cubes* are the oxygen atoms. Every divalent atom touches four oxygen atoms and nothing else. Every trivalent atom touches six oxygen atoms and nothing else. Every oxygen atom touches one divalent and three trivalent atoms. The distance between the centres of two neighbouring divalent atoms in magnetite is 3.60Å.

tures such as calcite, zinc blende, fluorspar, and iron pyrites, were analysed. On the other hand, since the arrangement of atoms in these crystals was known, it was possible to calculate the spacings of the reflecting planes and so to assign a definite wavelength to the characteristic lines in the spectrum. By using tubes with anticathodes of platinum, osmium, tungsten, nickel, and other metals, it became clear that each gave off a radiation containing characteristic lines which agreed in their properties with the K- or L-radiations first discovered by Barkla. Further, Whiddington had measured the energy of the cathode rays required to excite Barkla's K- and L-radiations. The results obtained with the spectrometer gave the frequency of these radiations, and my father was able to show that the product, of the frequency and Planck's constant *h,* was equal to the cathode-ray energy required to excite the rays; this was a first proof of the quantum law as applied to X-rays.
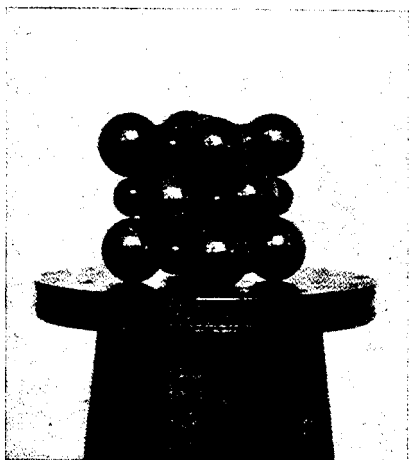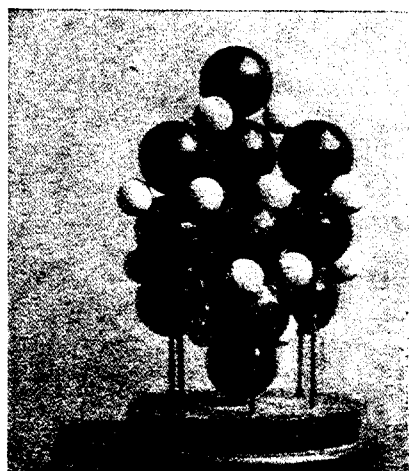
Fig. 8.

Fig. 9.

Fig. 8. *Rocksalt* (See also Fig. 1).
Fig. 9. *Calcite.* The *large dark ball* is the
calcium atom; *the small dark ball,* carbon;
and the *white ball,* oxygen.

Fig. 10.

Fig. 10. *Corundum* (Al_2O_3). The type of
symmetry is the same as that of calcite.
The axis is vertical. The *dark balls* repre-
sent aluminium, the *white balls,* oxygen.

These two lines of investigation, into X-ray spectra and into crystal struc-
ture, are the two great branches of research to which von Laue's discovery
led. Moseley was the first to make a survey of X-ray spectra. His famous
researches established the law which governs the number and order of the
elements. He found that, in passing from one element to the next in the
Periodic Table, there was a regular progression of the frequency in the K-and
L-radiations given out by the elements, and that its regularity was so great
that it was possible to assign with absolute certainty each element to its prop-
er place in the list, and to find the gaps where an element was not known.
Moseley's death in the war cut short his brilliant career at its outset. Since

then the technique of X-ray spectrometry has been very highly developed. No one has done more in this line than Prof. Siegbahn at your University of Lund, who has attained such a marvellous accuracy and delicacy in his measurement of X-ray spectra. The establishment of the origin of the K-, L-, and M-radiations first indicated by Kossel's relationships, and the examination of the absorption edges, where the absorbing power of an element, for different wavelengths, passes through a critical value, have been of vital importance in the study of atomic structure since they furnish direct evidence as to the amount of energy-change, when an electron passes from one stationary state to another in the interior of the atom. The refinement to which wavelength measurement can now be pushed has even made it possible to discover that there are small differences in the position of these absorption edges, when different chemical compounds of an element are used as absorbers, as Dr. Lindh has shown, and this suggests a new and most powerful method of examining the chemical composition of substances and the potential energy of valency bonds.

The examination of crystal structure, with the aid of X-rays has given us for the first time an insight into the actual arrangement of the atoms in solid bodies. The study of structure by means of a microscope is limited by the coarseness of the light which illuminates the object, for we can never hope

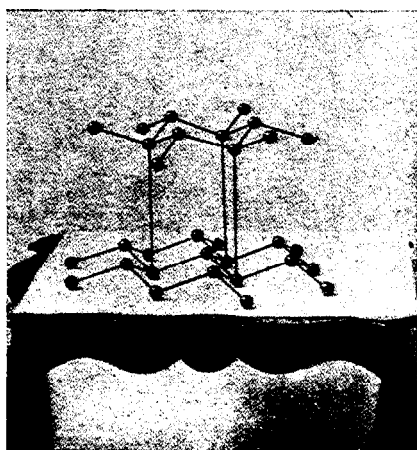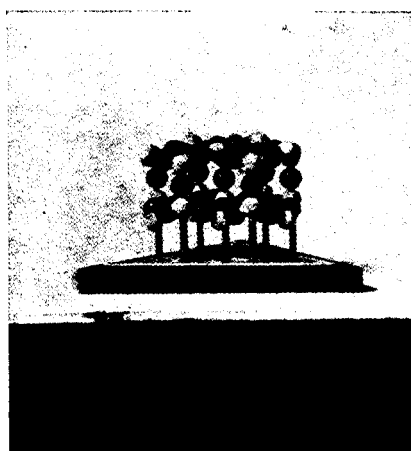
Fig. 11.   Fig. 12.

Fig. 11. *Graphite.*

Fig. 12. *Ice (H₂O).* The *white balls* represent the oxygen atoms, the *black balls* the hydrogen atoms. The oxygen atoms are arranged like those of carbon in diamond. Each hydrogen atom is situated midway between two oxygen atoms.

to see details smaller than the wavelength of the light. By using X-rays with their very short wavelengths, this limit of minuteness has at one step been decreased ten thousand times, for the wavelength of the X-rays is of a smaller order than the dimensions of the atomic structure. We are actually looking into the interior of the molecule and the atom with this fine-grained form of light.

The limits of the crystal pattern are arranged on a space lattice. Each limit is repeated over and over again in an identical fashion throughout the structure, at regular intervals in all directions. In analysing a crystal structure by X-rays, it is first necessary to find the dimensions of the unit cell of this space lattice, which has for its sides the primitive translation which the structure may be supposed to undergo in order to be brought into self-coincidence. It is a simple matter to achieve this. We find the angle at which a monochromatic beam of X-rays of known wavelength is reflected by the various faces of the crystal. Reflexion takes place only when the relation

$$n\lambda = 2d \sin \vartheta$$

is satisfied, and so the spacing d of the planes parallel to any face under examination can be found by measuring the angle ϑ. The dimensions of the unit cell can be found by measuring d for several faces. Having determined the dimensions of the unit cell, we can calculate how many atoms or molecules are contained within it, using as data the density of the crystal and the mass of each molecule.

The second step in analysis consists in the determination of the manner in which the atoms are grouped together to form each unit of the structure. It is here that the principal difficulty is experienced. The way in which the analysis is pursued may be illustrated by an analogy with the spectra obtained with a diffraction grating. It is well known that the form of the lines ruled on a grating has an influence on the relative intensity of the spectra which it yields. Some spectra may be enhanced, or reduced, in intensity as compared with others. Indeed, gratings are sometimes ruled in such a way that most of the energy is thrown into those spectra which it is most desirable to examine. The form of the line on the grating does not influence the positions of the spectra, which depend on the number of lines to the centimetre, but the individual lines scatter more light in some directions than others, and this enhances the spectra which lie in those directions.

The structure of the group of atoms which composes the unit of the crystal

grating influences the strength of the various reflexions in exactly the same way. The rays are diffracted by the electrons grouped around the centre of each atom. In some directions the atoms conspire to give a strong scattered beam, in others their effects almost annul each other by interference. The exact arrangement of the atoms is to be deduced by comparing the strength of the reflexions from different faces and in different orders.

In our early work we made certain assumptions in order to unravel the complex tangle which the reflexions from some crystals represented. We supposed that the diffraction took place at the centre of each atom, as if the whole effect were localized there. Further, we supposed that the effect of an atom was proportional to its atomic weight. Neither of these assumptions is more than very approximately true, as deeper analysis has shown. However, theory shows that the strength of the scattered beams varies so greatly with slight changes in the relative positions of the atoms, that these assumptions will serve to give an accurate determination of these positions. We analysed a number of simple crystals in this way, examples of which are given in the plates at the end of this address.

A single crystal is employed in the X-ray spectrometer. We used large crystals in our first experiments, reflecting from natural or artificially pre-pared faces. It is not essential to do this, however, for the ionization chamber is so sensitive a detector of X-radiation that small crystals a millimetre or two in breadth can be examined. In this case the rays are reflected through-out the whole volume of the crystal, which is not sufficiently thick to absorb them too much. A small crystal can be set at the centre of the instrument, adjusted so that a zone is parallel to the axis, and then turned round so that the reflexion of various faces is observed in turn. The X-ray spectrometer may be thus used in a manner very similar to that employed by a crystallo-grapher when he measures a crystal with a goniometer. It is a more search-ing method, however. The goniometer can only measure the angles between faces which have been developed on the crystal, whereas the X-ray spectro-meter measures the angles between planes of the crystal structure, and the spacings of the planes, although the crystal may have no regular external form.

In many cases it is impossible to obtain even small perfect crystals. The beautiful method of analysis initiated by Debye and Scherrer in Germany, and by Hull in America, has overcome this difficulty. In their method a monochromatic beam of X-rays is allowed to fall on a mass of crystalline powder. Some of the minute crystals will be set so as to reflect the rays for

every face and order, and so to give rise to a series of diffracted haloes which are recorded on a photographic plate. By means of this method, Hull has analysed the structure of a very large number of elements, including most of the metals. The method is admirably adapted to the study of compounds which do not form large crystals, but whose structure is very simple. By itself, it is not so well adapted to the analysis of complex crystals, since there is nothing to indicate which planes have given rise to the diffracted beams observed on the plate. Very often, however, a clue to the unravelling of the data can be got by examining the reflexion from an identified plane of a single small crystal; this gives us the key which enables us to assign the lines on the Debye photograph to the correct crystal planes.

The Debye method of crystal analysis has possibilities of development which have hardly been touched on as yet. A complex mixture of different crystals can be analysed, since each substance gives its characteristic series of haloes. This is an entirely new way of attacking such problems as the structure of alloys, or of minerals, since it tells us, not only what are the constituents, but how they are built up into solids; their crystallographic as well as their chemical structure.

A further development of the powder method which has proved to be most interesting is the study of colloidal particles. Scherrer has shown that particles of metals in the colloidal state consist of minute crystals, with a structure like that of large crystals; he has even formed an estimate of the size of the particles by observing the broadening of the haloes, this being due to a loss of resolving power owing to the small number of reflecting planes in any one particle.

There seems to be hardly any type of matter in the condition of a true solid which we cannot attempt to analyse by means of X-rays. For the first time the exact arrangement of the atoms in solids has become known; we can see how far the atoms are apart and how they are grouped. The importance of this consists in the light it throws on chemical composition. Very few crystals have yet been analysed by means of X-rays, and those that have been done are of simple composition, but as the knowledge of crystal structure increases we ought to get a far deeper insight into the nature of the forces which bind atoms together. One type of chemical binding has been already confirmed. In a structure such as that of sodium chloride (Fig. 1) the atoms of sodium and chlorine are not associated into chemical molecules, but are arranged alternately equidistant from several neighbours. This is explained by supposing that these atoms are ionized in the crystal structure, and that

the whole is held together by the attraction of oppositely charged ions. This is in accordance with the theories of Kossel on the constitution of compounds, and the work of Born and Landé has shown that we can make quantitative comparisons between the electrical potential energy of such an assemblage of ions, and the heat of formation of the solid from its elements. This is one of the first steps towards an explanation of chemical affinity in terms of familiar physical forces.

On the other hand, the chemical composition of a compound aids in the determination of its crystal structure. So many dispositions of the atoms are possible, in the more complex crystals, that one is at a loss where to begin in trying various arrangements in order to explain the X-ray diffraction effects. A knowledge of the most probable configuration of the atoms, and of the distances between them, is of the greatest assistance, however approximate it may be. This may perhaps be illustrated by the structures of the aromatic organic compounds, some of which my father has lately succeeded in analysing. The symmetry of the crystals of such substances as naphtalene, anthracene, and their derivatives is low, and there are a large number of atoms in the molecule, so that the analysis of their structures would be very difficult from first principles. However, it was assumed that the size of the benzene
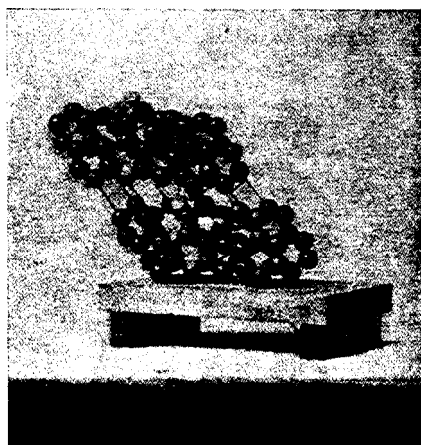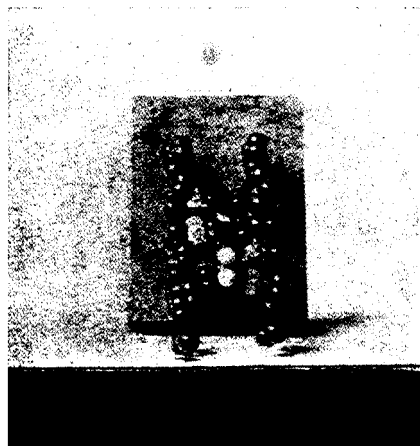

Fig. 13.

Fig. 14.

Fig.13. *Naphthalene (C₁₀H₈)*. The double rings of *grey balls* represent the double benzene rings of carbon atoms. The positions of the hydrogen atoms are indicated by the *black* and *white balls*.

Fig.14. *Naphthalene (C₁₀H₈)*. The same model as in Fig. 13, viewed perpendicularly to the C-axis.

rings in these crystals was approximately the same as that of the corresponding rings in diamond and graphite. With this assumption, the data on the size of the unit cell for all these compounds fell into relationship with each other. The benzene ring could be treated as a single unit, and space had to be found in the crystal structure for one or more to be packed into each unit cell. Probably the solutions of many other complex crystals, which appear almost hopeless at present, will be made along similar lines.

Finally, there is a still deeper application of the X-ray analysis, to the structure of the atom itself. Since the wavelength of the X-rays is less than the "atomic diameter", as it is somewhat vaguely termed, and since the rays are presumably diffracted by the electrons in the atom, we ought to be able to get some idea of the distribution of these electrons in the same way that we draw conclusions as to the grouping of the atoms. Interference between the waves scattered by the electrons must take place. In order to study this question, a much closer analysis of the mechanism of X-ray reflexion must be made. Many workers have attacked this problem, amongst them Darwin in England, Debye in Germany, Compton in America. We have been trying to make some accurate quantitative determinations of the strength of X-ray reflection, the object in view being the measurement of the amount of radiation scattered by an atom in all directions when an X-ray beam passes over it. The whole subject bristles with difficulties, and the assumptions on which the theory of reflexion rests have not been exhaustively proved. On the other hand there seems to be a prospect that the method will prove a valid way of testing various models proposed for the atom, since the way, in which these models should diffract the rays, can be calculated, and compared with that which is actually observed.

I have only given in this account a very brief description of the many lines of investigation which have arisen from von Laue's discovery. I wish that there were more contributions of my own to this subject which I could have described to you, to justify the supreme compliment which you paid me in giving me your award, but the war interrupted work for so many years, and since then there has been so much reorganization of all university work in England that research has been difficult to achieve. I will conclude, then, in expressing my thanks to you for giving me this opportunity of addressing you, and my gratitude for all which I owe to you.