Self Portrait

WLB Jan 65

WILLIAM LAWRENCE BRAGG

The Dawn of X-ray Crystallography

Introduction

Following the discovery of X-rays by Wilhelm Roentgen in 1895, a key question that needed to be answered was whether these rays were made up of corpuscles or of waves. Despite many attempts to resolve this, it remained unsolved until the spring of 1912. Some experiments, such as the Wilson cloud chamber studies, indicated a particulate nature. On the other hand, a slight spreading of the X-ray beam, when it was passed through a narrow slit, suggested diffraction, which would imply waves. Based on a conversation with a postgraduate student, Paul Ewald in Munich, Max Laue[$] proposed an experiment to show that, if they were wave-like, X-rays should be diffracted by a crystal. The then head of the institute, Arnold Sommerfeld, was reluctant to allow any time to be spent pursuing such an idea, arguing, according to many accounts, that any diffraction effects would be eliminated by the thermal motion of the atoms in the crystal[*]. Nonetheless, it seems that Laue got Paul Knipping and Walter Friedrich to try out the experiment in April 1912, and after several thwarted attempts they obtained spots on a photographic plate when a beam of X-rays was incident on a crystal of copper sulfate. Subsequently they obtained even better photographs with ZnS and diamond. This demonstrated, for the first time, that X-rays can be diffracted by crystals, a sign that they should therefore be treated as waves, and this work was published in June and July of that year. Laue subsequently received the Nobel Prize for this momentous discovery in 1914, although it is interesting to note that it was not awarded to Friedrich and Knipping. However, despite the fact that Laue had derived the correct diffraction equations, he was unable to account for the exact arrangement of the spots, mainly because he made a number of incorrect assumptions about the diffraction process and the structures of crystals.

Working in Leeds around that time, William Henry Bragg (hereafter WHB) was convinced that X-rays were particle-like in nature, and so, with his son William Lawrence Bragg (hereafter WLB), set about showing how Laue's patterns could be explained by channelling of particles through 'avenues' within the crystals. However, WLB became convinced that the correct explanation was actually one in which X-rays consisted of waves rather than particles. On November 11th 1912 J.J. Thomson presented WLB's paper on this to the Cambridge Philosophical Society. Shortly thereafter WHB realised the importance of WLB's insight and WLB recognised the

[$] In June 1913 Laue's father was enobled and thenceforth the name became von Laue.

[*] This story about thermal motion has been disputed. It has been proposed that it is more likely that Sommerfeld was opposed to the experiment, because he would have known that Laue was mistaken in his thinking that interference could arise from secondary X-rays emanating from atoms within the crystal. See M. Eckert, *Acta Cryst.*, **A30**, 30-39 (2012).

value of WHB's new X-ray spectrometer (first reported Jan 23rd, Nature, 1913), and father and son then collaborated to found the new field. (Note that it was not until 1924 that de Broglie proposed the idea of wave-particle duality, and so in a sense WHB was ahead of his time in his original belief in the corpuscular nature of X-rays).

WLB's paper subsequently appeared in print in February 1913[**]. The importance of this work cannot be overstated, for it heralded a revolution in the scientific understanding of crystals and their atomic arrangements. This discovery led to many of the most important scientific achievements of the last century, and these continue to the present day. This paper was the beginning of the field of X-ray crystallography, a subject that has enabled us to establish the complete structures of crystals, starting from the very simple to the most complex materials, such as proteins, viruses and the molecule that forms the very essence of life, namely DNA.

Around 20 or so Nobel Prizes have been awarded for research that has used the ideas described in this paper. Modern genetics, medicine and the study of materials owe an incalculable debt to WLB, who at the astonishingly young age of 22, made a discovery that has changed our understanding of the world around us. Both father and son shared the 1915 Nobel Prize for their work, with WLB remaining to the present day the youngest Nobel Prize winner ever.

In order to show precisely what WLB had achieved, a copy of the original paper is enclosed together with brief notes indicating some of the important points. Every time one reads this paper one cannot fail to be struck by the beautiful simplicity of WLB's treatment and evidence of the mind of a genius. Not bad for a mere 22 year old! We hope you too will be equally impressed by this seminal publication.

Mike Glazer   Emeritus Professor of Physics (Oxford University) and Visiting Professor (Warwick University)
John Jenkin   Honorary Associate, Philosophy Program, La Trobe University, Australia

[**] Some authors quote the reference year for this publication as 1913 while others 1912. Confusingly, Volume XVII (17) has a date range of 28 October 1912 to 18 November 1914, and is in five parts. The parts have dates according to when the papers were either delivered orally or accepted for publication, and so, depending on the meaning of "publication" as opposed to "printed" it can be argued that the correct reference is *Proc. Camb. Phil. Soc.*, **XVII (I)**, 1912, pp. 43-57. Note that WLB published a brief report of the Cambridge Philosophical Society meeting, including his idea of reflection from planes, on December 5th 1912 in Nature, Volume **90**, page 402.

We reproduce here for the first time, by kind permission of the Cambridge Philosophical Society, the original agenda and minutes taken during the November 11th 1912 meeting of the Society.

CAMBRIDGE PHILOSOPHICAL SOCIETY.

The next Meeting of the Society will be held on Monday, 11 November, at 4.30 o'clock, in the Cavendish Laboratory. It is expected that the following COMMUNICATIONS will be made:

I. By Professor Sir J. J. THOMSON:
   On the theory of the motion of charged ions through gases.

II. By Dr G. F. C. SEARLE:
   On a simple method of determining the viscosity of air.

III. By Mr R. WHIDDINGTON:
   Note on the Röntgen Radiation from Cathode particles traversing a gas.

IV. By W. L. BRAGG, B.A.:
   The Diffraction of Short Electromagnetic Waves by a Crystal.
   (Communicated by Professor Sir J. J. THOMSON.)

V. By H. E. WATSON:
   Experiments on the Electrical Discharge in Helium and Neon.
   (Communicated by Professor Sir J. J. THOMSON.)

VI. By Mr H. C. POCKLINGTON:
   Some Diophantine Impossibilities.

VII. By Mr G. N. WATSON:
   A class of Integral Functions defined by Taylor's Series.

   [The last three Papers will be taken as read.]

VIII. By A. T. Berry, B.A.
   Notes on the Volatilisation of certain Binary alloys in high vacua.

At a Meeting of the Society held on Monday
November 11ᵗʰ at 4·30 p.m. in the Cavendish Laboratory,
Professor Sir J.J. Thomson O.M. in the Chair

(1) The minutes of the previous meeting were
read and confirmed.

(2) Mr J. Gray B.A.   King's College
Mr H. Hartridge M.A. King's College
were proposed as Fellows of the Society

(3) Mr G. B. Horny   Christ's College
Mr H. Smith   Emmanuel College
were elected for Associates of the Society.

(4) The following communications were made :—

I By Professor Sir J.J. Thomson:
On the theory of the motion of charged ions
through gases.

II By Dr G.F.C. Searle:
On a simple method of determining the
viscosity of air

III By Mr R. Whiddington:
Note on the Röntgen Radiation from Cathode
particles traversing a gas

IV By W.L. Bragg, B.A.:
The diffraction of short electromagnetic waves
by a crystal

THE DIFFRACTION OF SHORT ELECTROMAGNETIC WAVES BY A CRYSTAL

BY

W. L. BRAGG, B.A., Trinity College.

The Diffraction of Short Electromagnetic Waves by a Crystal. By W. L. BRAGG, B.A., Trinity College. (Communicated by Professor Sir J. J. Thomson.)

[*Read* 11 November 1912.]

[PLATE II.]

Herren Friedrich, Knipping, and Laue have lately published a paper entitled 'Interference Phenomena with Röntgen Rays*,' the experiments which form the subject of the paper being carried out in the following way. A very narrow pencil of rays from an X-ray bulb is isolated by a series of lead screens pierced with fine holes. In the path of this beam is set a small slip of crystal, and a photographic plate is placed a few centimetres behind the crystal at right angles to the beam. When the plate is developed, there appears on it, as well as the intense spot caused by the undeviated X-rays, a series of fainter spots forming an intricate geometrical pattern. By moving the photographic plate backwards or forwards it can be seen that these spots are formed by rectilinear pencils spreading in all directions from the crystal, some of them making an angle of over 45° with the direction of the incident radiation.

When the crystal is a specimen of cubical zinc blende, and one of its three principal cubic axes is set parallel to the incident beam, the pattern of spots is symmetrical about the two remaining axes. This pattern is shown in Plate II. Laue's theory of the formation of this pattern is as follows. He considers the molecules of the crystal to form a three-dimensional grating, each molecule being capable of emitting secondary vibrations when struck by incident electromagnetic waves from the X-ray bulb. He places the molecules in the simplest possible of the three cubical point systems, that is, molecules arranged in space in a pattern whose element is a little cube of side 'a,' with a molecule at each corner. He takes coordinate axes whose origin is at a point in the crystal and which are parallel to the sides of the cubes. The incident waves are propagated in a direction parallel to the z axis, and on account of the narrowness of the beam the wave surfaces may be taken to be parallel to the xy plane. The spots are considered to be interference maxima of the waves scattered by the orderly arrangement of molecules in the crystal. In order to get an interference maximum in the direction

* *Sitzungsberichte der Königlich Bayerischen Akademie der Wissenschaften.* June 1912.

whose cosines are α, β, γ, for incident radiation of wave-length λ, the following equations must be satisfied

$$a\alpha = h_1\lambda, \quad ap = h_2\lambda, \quad a(1-\gamma)=h_3\lambda \ldots\ldots\ldots(1)$$

where h_1 h_2 h_3 are integers.

These equations express the condition that the secondary waves of wave-length λ from a molecule, considered for simplicity as being at the origin of coordinates, should be in phase with those from its neighbours along the three axes, and that therefore the secondary waves from all the molecules in the crystal must be in phase in the direction whose cosines are α β γ.

The distance of the crystal from the photographic plate in the experiment was 3·56 cm. The pencil of X-rays on striking the crystal had for cross-section a circle of diameter about a millimetre, and the dimensions of the spots are of the same order. The plate of crystal was only ·5 millimetre thick. It is thus easy to calculate with considerable accuracy from the position of a spot on the photographic plate the direction cosines of the pencil to which it corresponds, since the pencils of rays may be all taken as coming from the centre of the crystal. Laue found, on doing this for each spot, that as a matter of fact the values for α β $1-\gamma$ so obtained were in the numerical ratio of three small integers h_1 h_2 h_3 as they should be by equations (1).

For instance, a spot appears on the photographic plate whose coordinates referred to the x and y axes are

$$x = \cdot 28 \text{ cm.}, \quad y = 1\cdot 42 \text{ cm.}$$

The distance of the crystal from the photographic plate, 3·56 cm., gives z.

Thus since
$$\alpha : \beta : \gamma :: x : y : z$$

$$\frac{\alpha}{\cdot 28} = \frac{\beta}{1\cdot 42} = \frac{\gamma}{3\cdot 56} = \frac{1}{\sqrt{(\cdot 28)^2 + (1\cdot 42)^2 + (3\cdot 56)^2}} = \frac{1}{3\cdot 83}.$$

Thus
$$\frac{\alpha}{\cdot 28} = \frac{\beta}{1\cdot 42} = \frac{1-\gamma}{\cdot 27},$$

or
$$\alpha : \beta : 1-\gamma :: 1 : 5 : 1.$$

Laue considers some thirteen of the most intense spots in the pattern. Owing to the high symmetry of the figure, the whole pattern is a repetition of that part of it contained in an octant. Thus these thirteen represent a very large proportion of all the spots in the figure. For these spots he obtains corresponding integers h_1 h_2 h_3 which are always small, the greatest being the number 10. But even if one confines oneself to integers less than 10, there are a great many combinations of h_1 h_2 h_3 which might

give spots on the photographic plate which are in fact not there, and there is no obvious difference between the numbers h_1 h_2 h_3 which correspond to actual spots, and those which are not represented.

To explain this Laue assumes that only a few definite wavelengths are present in the incident radiation, and that equations (1) are merely approximately satisfied.

Considering equations (1) it is clear that when h_1 h_2 h_3 are fixed $\dfrac{\lambda}{a}$ can only have one value. However if h_1 h_2 h_3 are multiplied by an integral factor p, equations (1) can still be satisfied, but now by a wave-length $\dfrac{\lambda}{p}$. By adjusting the numbers h_1 h_2 h_3 in this way, Laue accounts for all the spots considered by means of five different wave-lengths in the incident radiation. They are

$$\lambda = {\cdot}0377a$$
$$\lambda = {\cdot}0563a$$
$$\lambda = {\cdot}0663a$$
$$\lambda = {\cdot}1051a$$
$$\lambda = {\cdot}143a.$$

For instance, in the example given above, where it was found that

$$\alpha : \beta : 1-\gamma :: 1 : 5 : 1$$

these numbers are multiplied by 2, becoming 2.10.2. Then they can be assigned to a wave-length

$$\frac{\lambda}{a} = {\cdot}037,$$

approximately equal to the first of those given above.

However, this explanation seems unsatisfactory. Several sets of numbers h_1 h_2 h_3 can be found giving values of $\dfrac{\lambda}{a}$ approximating very closely to the five values above and yet no spot in the figure corresponds to these numbers. I think it is possible to explain the formation of the interference pattern without assuming that the incident radiation consists of merely a small number of wave-lengths. The explanation which I propose, on the contrary, assumes the existence of a continuous spectrum over a wide range in the incident radiation, and the action of the crystal as a diffraction grating will be considered from a different point of view which leads to some simplification.

Regard the incident light as being composed of a number of independent pulses, much as Schuster does in his treatment of the action of an ordinary line grating. When a pulse falls on a plane it is reflected. If it falls on a number of particles scattered over a plane which are capable of acting as centres of disturbance when struck by the incident pulse, the secondary waves from them will build up a wave front, exactly as if part of the pulse had been reflected from the plane, as in Huygen's construction for a reflected wave.

The atoms composing the crystal may be arranged in a great many ways in systems of parallel planes, the simplest being the cleavage planes of the crystal. I propose to regard each interference maximum as due to the reflection of the pulses in the incident beam in one of these systems. Consider the crystal as divided up in this way into a set of parallel planes. A minute fraction of the energy of a pulse traversing the crystal will be reflected from each plane in succession, and the corresponding interference maximum will be produced by a train of reflected pulses. The pulses in the train follow each other at intervals of $2d \cos \theta$, where θ is the angle of incidence of the primary rays on the plane, d is the shortest distance between successive identical planes in the crystal. Considered thus, the crystal actually 'manufactures' light of definite wave-lengths, much as, according to Schuster, a diffraction grating does. The difference in this case lies in the extremely short length of the waves. Each incident pulse produces a train of pulses and this train is resolvable into a series of wave-lengths λ, $\frac{\lambda}{2}$, $\frac{\lambda}{3}$, $\frac{\lambda}{4}$ etc. where $\lambda = 2d \cos \theta$.

Though to regard the incident radiation as a series of pulses is equivalent to assuming that all wave-lengths are present in its spectrum, it is probable that the energy of the spectrum will be greater for certain wave-lengths than for others. If the curve representing the distribution of energy in the spectrum rises to a maximum for a definite λ and falls off on either side, the pulses may be supposed to have a certain average 'breadth' of the order of this wave-length. Thus it is to be expected that the intensity of the spot produced by a train of waves from a set of planes in the crystal will depend on the value of the wave-length, viz. $2d \cos \theta$. When $2d \cos \theta$ is too small the successive pulses in the train are so close that they begin to neutralize each other and when again $2d \cos \theta$ is too large the pulses follow each other at large intervals and the train contains little energy. Thus the intensity of a spot depends on the energy in the spectrum of the incident radiation characteristic of the corresponding wave-length.

Another factor may influence the intensity of the spots. Consider a beam of unit cross-section falling on the crystal. The

strength of a pulse reflected from a single plane will depend on the number of atoms in that plane which conspire in reflecting the beam. When two sets of planes are compared which produce trains of equal wave-length it is to be expected that if in one set of planes twice as many atoms reflect the beam as in the other set, the corresponding spot will be more intense. In what follows I have assumed that it is reasonable to compare sets of planes in which the same number of atoms on a plane are traversed by unit cross-section of the incident beam, and it is for this reason that I have chosen the somewhat arbitrary parameters by which the planes will be defined. They lead to an easy comparison of the effective density of atoms in the planes. The effective density is the number of atoms per unit area when the plane with the atoms on it is projected on the xy axis, perpendicular to the incident light.

Laue considers that the molecules of zinc-blende are arranged at the corners of cubes, this being the simplest of the cubical point systems. According to the theory of Pope and Barlow this is not the most probable arrangement. For an assemblage of spheres of equal volume to be in closest packing, in an arrangement exhibiting cubic symmetry, the atoms must be arranged in such a way that the element of the pattern is a cube with an atom at each corner and one at the centre of each cube face. With regard to the crystal of zinc-blende under consideration zinc and sulphur being both divalent have equal valency volumes and their arrangement is probably of this kind. It will be assumed for the present that the zinc and sulphur atoms are identical as regards their power of emitting secondary waves.

Take the origin of coordinates at the centre of any atom, the axes being parallel to the cubical axes of the crystal. The distance between successive atoms of the crystal along the axes is taken for convenience to be $2a$.

All atoms in the xz plane will have coordinates

$$pa \quad o \quad qa$$

where p and q are integers and $p + q$ is even. See fig. 1 in text.

The same holds for atoms in the yz plane. Therefore any reflecting plane may be defined by saying that it passes through the origin, and the centres of atoms

$$pa \quad o \quad qa$$
$$o \quad ra \quad sa$$

For instance, the plane on which the triangle OAB lies passes through the origin and

$$a \quad o \quad 3a$$
$$a \quad o \quad a$$

The planes can now be classified by the corresponding values of p, q, r, s as parameters.

The direction cosines of a plane $p\ q\ r\ s$ will be

$$\frac{rq}{\sqrt{p^2s^2+q^2r^2+p^2r^2}},\quad \frac{ps}{\sqrt{p^2s^2+q^2r^2+p^2r^2}},\quad \frac{-pr}{\sqrt{p^2s^2+q^2r^2+p^2r^2}}.$$

If these are called $l\ m\ n$ the direction cosines of the reflected beam are
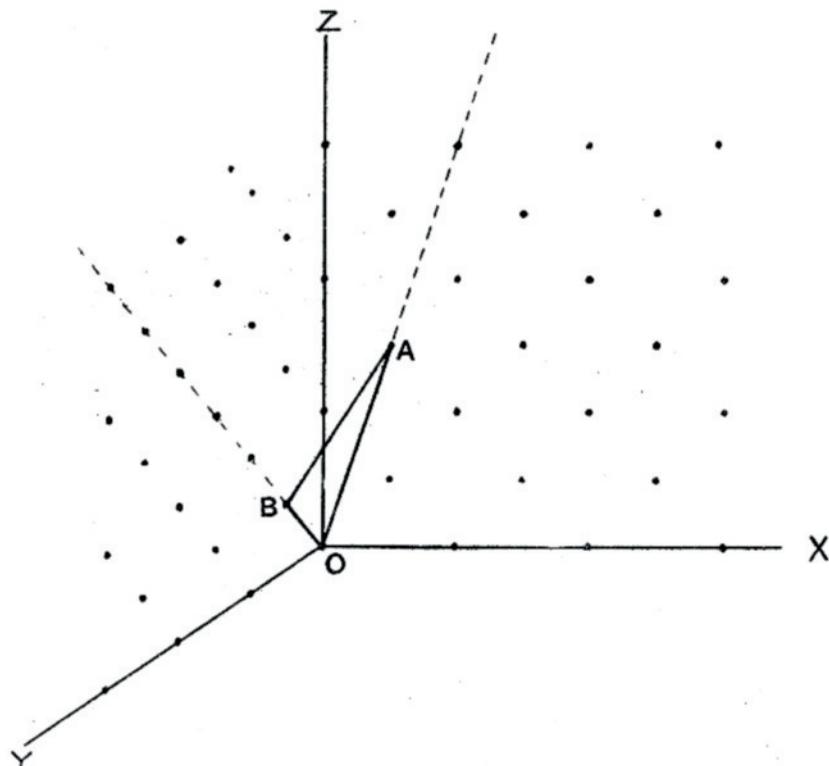
$$2ln,\quad 2mn,\quad 2n^2-1,$$

Fig. 1.

and the position of the interference maximum on the photographic plate can be found in terms of these quantities.

The corresponding wave-length is $2d \cos\theta$ where d is the perpendicular distance between successive planes. Now θ is the angle of incidence, therefore $\cos\theta = n$ above. It is easier to find the intercepts which successive planes cut off on the z axis, than their perpendicular distance apart. Calling these intercepts l, then

$$\lambda = 2d \cos\theta = 2\,.\,l\cos\theta\,.\,\cos\theta = 2ln^2.$$

Consider the atoms as arranged in vertical rows parallel to the z axis in the figure. A plane for which $p=1$ and $r=1$ passes through one atom in every one of these vertical rows (see fig. 3). Therefore the next plane to it passes through a set of atoms all $2a$ above the corresponding atoms in the first plane. Thus for this set of planes, $l=2a$ and the wave-length $\lambda = 4an^2$. The effective density of atoms on such a set of planes is the greatest possible.

If $p=1$, $r=2$, each plane now passes through atoms in one half of the vertical rows. For instance, the plane through the origin contains no atoms in those vertical rows for which r is odd. The successive planes must cut the z axis at intervals $\dfrac{2a}{2}$, since the effective density of atoms in each is half as great as before and the whole number of atoms in unit volume of the crystal remains constant. Similarly if $p=1$, $r=3$ $l=\dfrac{2a}{3}$ and so forth.

In the general case $l = \dfrac{2a}{\text{L.C.M. of } p \text{ and } r}$.

In the tables given below planes with the same effective density of atoms on them, and therefore the same values of l, are grouped together.

The position of the spot reflected by each system of planes considered has been calculated, also the wave-length of the reflected train expressed for convenience in the form $\dfrac{a}{\lambda}$, and when in the photograph a spot is visible in the position calculated, its intensity is denoted by star according to an arbitrary scale.

<center>❋　　❊　　＊　　＋　　●</center>

When no spot appears in the calculated position, I have put 'invisible' opposite that plane.

There is no need to go any further than the set for which $l=\dfrac{2a}{4}$, to obtain all the spots in the photograph. Indeed only one spot is given by this last set.

Only one spot on the plate is to be assigned to planes of this class. It is curious that the value of $\dfrac{a}{\lambda}$ corresponding to this spot should be as great as 11·2. It is noticeable in the photograph that all spots at any distance from the centre of the pattern tend to become very faint, and the values of p, q, r, s which do give a spot in Table IV are the only ones to be found giving a spot at all near the centre. In the first three tables the parameters

corresponding to a value of $\frac{a}{\lambda}$ between 6 and 9 are represented by the most intense spots.

Every spot in the photograph is accounted for in the following Tables. I think it is evident that the sets of planes which actually reflect spots can be arranged in a very complete series with few or no gaps. Though at first sight it may appear that in the

TABLE I.

Planes for which $p = 1$, $r = 1$, $l = 2a$, $\lambda = 4an^2$.

p	q	r	s	$\frac{a}{\lambda}$	Intensity	h_1	h_2	h_3
1	1	1	3	2·8	*	1	3	1
1	1	1	5	6·8	❋	1	5	1
1	1	1	7	12·8	*	1	7	1
1	1	1	9	20·8	Invisible	1	9	1
1	3	1	1	2·8	*	3	1	1
1	3	1	3	4·8	*	3	3	1
1	3	1	5	8·8	❋	3	5	1
1	3	1	7	14·8	+	3	7	1
1	3	1	9	22·8	Invisible	3	9	1
1	5	1	1	6·8	❋	5	1	1
1	5	1	3	8·8	❋	5	3	1
1	5	1	5	12·8	*	5	5	1
1	5	1	7	18·8	Invisible	5	7	1
1	7	1	1	12·8	*	7	1	1
1	7	1	3	14·8	+	7	3	1
1	7	1	5	18·8	Invisible	7	5	1
1	9	1	1	20·8	Invisible	9	1	1

Range of values of $\frac{a}{\lambda}$, all possible up to 15.

tables the parameters are selected in a somewhat arbitrary way, they are in reality the simplest possible. For instance, in Table III the first values for p, q, r, s considered are 1, 1, 3, 5. This is so because '$r + s$' must be positive. If $r = 1$, s must be odd.

1, 1, 3, 1 and 1, 1, 3, 3 would reflect the beam so as to miss the photographic plate. 1, 1, 3, 5 and 1, 1, 3, 7 are considered. 1, 1, 3, 9 has already been considered as 1, 1, 1, 3, and 1, 1, 3, 11 gives a value for the wave-length outside the 'visible' range.

In fig. 3, Plate II, is given a photograph of the interference pattern which Laue obtained. In fig. 4, Plate II, the key to the pattern has been drawn, showing in what planes the spots are to be considered as reflected.

TABLE II.

Planes for which L.C.M. *of p and* $r = 2$, $l = a$, $\lambda = 2an^2$.

p	q	r	s	$\dfrac{a}{\lambda}$	Intensity	h_1	h_2	h_3
1	1	2	4	3	•	2	4	2
1	1	2	8	9	*	2	8	2
1	1	2	12	19	Invisible	2	12	2
2	4	2	0	2·5	Invisible	4	0	2
2	4	2	4	4·5	•	4	4	2
2	4	2	8	10·5	• ?	4	8	2
1	3	2	0	5	*	6	0	2
1	3	2	4	7	*	6	4	2
1	3	2	8	13	• ?	6	8	2
2	8	2	0	8·5	•	8	0	2
2	8	2	4	10·5	• ?	8	4	2
1	5	2	0	13	Invisible	10	0	2

Consider a reflecting plane which passes through the atom at the origin and a neighbouring atom, let us suppose the atom whose coordinates are a, o, a. As the plane is turned about the line through these two points the reflected beam traces out a circular cone, which has for axis the line joining the two points and for one of its generators the incident beam. This cone cuts the photographic plate in an ellipse. If the atom through which the plane passes is in the xz plane as above, the ellipse touches the y axis on the photographic plate at the origin. Now take a plane passing through the origin and a point 0, a, $3a$. The

TABLE III.

Planes for which L.C.M. *of p and* $r = 3$, $l = \dfrac{2a}{3}$, $\lambda = \dfrac{4an^2}{3}$.

p	q	r	s	$\dfrac{a}{\lambda}$	Intensity	h_1	h_2	h_3
1	1	3	5	3·6	Invisible	3	5	3
1	1	3	7	5·6	*	3	7	3
1	1	3	11	11·6	Invisible	3	11	3
3	5	3	5	4·9	Invisible	5	5	3
3	5	3	7	6·9	*	5	7	3
3	5	3	11	12·9	Invisible	5	11	3
3	7	3	1	4·9	Invisible	7	1	3
3	7	3	5	6·9	*	7	5	3
3	7	3	7	8·9	*	7	7	3
3	7	3	11	14·9	Invisible	7	11	3
1	3	3	1	7·6	*	9	1	3
1	3	3	5	9·6	+	9	5	3
1	3	3	7	11·6	Invisible	9	7	3

Range of values of $\dfrac{a}{\lambda}$, $5\cdot6 = 9\cdot6$.

TABLE IV.

Planes for which the L.C.M. *of p and* $r = 4$, $l = \dfrac{2a}{4}$,

$$\lambda = \dfrac{4an^2}{4} = an^2.$$

p	q	r	s	$\dfrac{a}{\lambda}$	Intensity	h_1	h_2	h_3
1	1	4	10	8·2	Invisible	4	10	4
1	1	4	14	16·2	Invisible	4	14	4
2	4	4	10	11·2	+	8	10	4
1	3	4	6	12·2	Invisible	12	6	4

locus of the reflected spot as it turns is again an ellipse, which now touches the x axis. The intersections of the two ellipses will give the position of a spot reflected by a plane passing through all three points, the origin, the point $a, 0, a$, and the point $0, a, 3a$.

The ellipses are drawn in the figure, and the plane corresponding to any spot can be found by noting the ellipses at the intersection of which the spot lies. Only those ellipses have been drawn which give the points in Table I. It will be seen that a very large proportion of the spots in the photograph lie at the intersection of these.

The analysis involved in this way of regarding the interference phenomena must be fundamentally the same as that employed by Laue. In fig. 1, suppose the phase difference between vibrations from successive atoms along the three axes, when waves of wavelength λ fall on the crystal, to be $2\pi h_1$, $2\pi h_2$, $2\pi h_3$. Then in order that the vibrations from those atoms, which are arranged in the figure at the centres of the cube faces, should also be in phase, one must have

$$\frac{h_1}{2} - \frac{h_3}{2} = \text{an integer}, \qquad \frac{h_2}{2} - \frac{h_3}{2} = \text{an integer}.$$

This condition is simply expressed by saying that h_1, h_2, h_3 must all be even or all odd integers. When h_1, h_2, h_3 are given, the value of λ follows from

$$\frac{\lambda}{2a} = \frac{2h_3}{\sqrt{h_1{}^2 + h_2{}^2 + h_3{}^2}},$$

since here $2a$ has been taken as the distance between neighbouring molecules along the three axes.

If the three simplest values of h_1, h_2, h_3 for a spot on the plate are not all odd, or all even, then these numbers must be doubled to make them even and the wave-length accordingly halved.

When this is done, it can be seen that for each value of h_3 there is a series of values of h_1 and h_2. These numbers all give spots in the photograph if the corresponding value of $\frac{a}{\lambda}$ lies within a certain range. The smaller the number h_1, the larger is the range of $\frac{a}{\lambda}$ for which spots are visible. Spots whose $\frac{a}{\lambda}$ lies near the extremity of the range are very faint, those whose $\frac{a}{\lambda}$ is in the middle of the range are intense. In the tables the values of h_1, h_2, h_3 corresponding to each spot are set down.

It is quite probable that the qualitative explanation put forward here to account for the intensities of the spots is not the right one, other explanations being possible. For instance, one might substitute for the factor termed 'effective density' above, one which expressed the fact that, other things being equal, spots nearer the centre of the pattern were more intense than those farther out. This, together with the right curve for the distribution of energy in the spectrum of the incident radiation, could be made to account for the intensities quite reasonably. This does not vitiate the conclusion that the spots in the pattern represent a series which is complete, and characteristic of a cubical crystalline arrangement. The other arrangements of cubical point systems cannot, as far as I can see, give such a complete series. The other possible arrangements have for elements of their pattern (1) a cube with a molecule or atom at each corner, the arrangement which Laue pictured, or (2) a cube with a molecule at each corner and one at the centre. Neither arrangement will fit the system of planes given above. It is only the third point system, the element of whose pattern has a molecule at each corner and one at the centre of each cube face, which will lend itself to the system of planes found to represent spots in the photograph.

This last system, seeing that it forms an arrangement of the closest possible packing, is according to the results of Pope and Barlow the most probable one for the cubic form of zinc sulphide.

In one of the photographs taken by Messrs Friedrich and Knipping the crystal was so oriented that the direction of the incident radiation made equal angles with the three rectangular axes of the crystal. In this case a figure is obtained in which the pattern is a repetition of the spots contained in a sector of angle $\frac{\pi}{6}$. Regarding the spots as reflections of the incident beam in planes as before, these planes can be found almost as easily as those which reflect the spots in the square pattern, and indeed in many cases the planes are identical. I will not give the calculations here, but one point is of especial interest. A photograph was taken of the crystal oriented so that the pattern obtained was perfectly symmetrical. The crystal was then tilted through 3° about a line perpendicular to the incident beam and to one of the cubical axes. This distorted the pattern considerably, but corresponding spots in the two patterns are easily to be recognised. The points which I wish to consider especially are the following.

In the first place, the spots in the distorted pattern are all displaced exactly as would be expected if they were reflections in planes fixed in the crystal. For instance, when the reflecting plane contains the line, about which the crystal was tilted through 3°, it can be ascertained that the movement of the spot

corresponds to a deviation of the reflected beam through 6°. This alone is, I think, strong evidence that the wave-length λ is elastic, and not confined to a few definite values, and that equations (1) are satisfied rigorously and not merely approximately.

Besides the distortion of the figure due to the tilting of the crystal, a very marked alteration in the intensity of the spots is to be noticed. This is especially marked for those spots which are near the centre of the pattern, but not on or near the axis about which the crystal is tilted. This is probably due to the fact that for these spots a considerable change in wave-length has taken place.

When the angle of incidence θ of the primary beam on a set of reflecting planes varies, the value of $2d \cos \theta$ is altered and the alteration for the same $\delta\theta$ is greater the greater θ is.

One spot in particular changes from being hardly visible in the symmetrical pattern to being by far the most intense when the crystal is tilted. It is the spot reflected in a plane passing through the origin and

$$3a, \ 0, \ a; \quad 0, \ 3a, \ a.$$

Planes parallel to this have for d, the shortest distance between successive planes, the value $\dfrac{4a}{\sqrt{11}}$. It can easily be calculated from the position of the spot that the value of $\cos \theta$ changes from ·19 to ·12 when the crystal is tilted. This corresponds to a change in the value of $\dfrac{a}{\lambda}$ from 4·3 to 6·5, and it was found before for the square pattern that spots corresponding to the former wave-lengths were weak, those corresponding to the latter intense.

A curious feature of the photographs may be explained by regarding the spots as formed by reflection. As the distance of the photographic plate from the crystal is altered, the shape of each individual spot varies. At first round, they become more and more elliptical as the plate is moved further away. A reason for this is found in the following. If the incident beam is not perfectly parallel, but slightly conical, rays will strike the crystal at slightly different angles. Regard the crystal as a set of reflecting planes perpendicular to the plane of the paper (fig. 2). The rays striking the reflecting planes on the upper part of the crystal on the whole meet them at a less angle of incidence than those striking the planes at the bottom; the latter are deflected more, and the rays tend on reflection to come to a focus in a horizontal line. On the other hand, rays deviating from the axial direction in a horizontal plane diverge still more after reflection. Thus as the plate is removed from the crystal, the spots up to a certain distance become more and more elliptical.

The atoms of a crystal may be arranged in 'doubly infinited' series of parallel rows, as well as in 'singly infinite' series of planes. The incident pulse falls on atom after atom in one of these rows, if the row is not parallel to the wave front, and secondary waves are emitted, one from each atom, at definite time intervals. Along any direction lying on a certain circular cone with the row of atoms as axis, these secondary waves will be all in phase, one generator of the cone being, of course, parallel to the direction of the incident radiation. If the row of atoms makes a small angle with the direction, this cone with vertex at the crystal slip may now be considered to cut the photographic plate in an almost circular ellipse passing through the big central
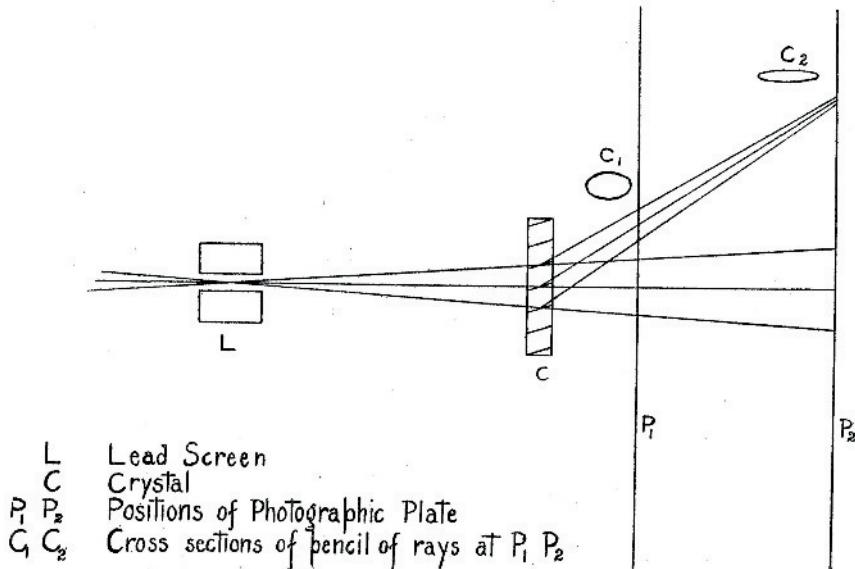

L	Lead Screen
C	Crystal
$P_1 P_2$	Positions of Photographic Plate
$C_1 C_2$	Cross sections of pencil of rays at $P_1 P_2$

Fɪɢ. 2.

spot. Drawing the ellipses which correspond to the most densely packed rows of the crystal, a spot is to be expected at the intersection of two ellipses, for this means that pulses from a doubly infinite set of atoms are in that direction in agreement of phase. Thus it ought to be possible to arrange the spots in the photograph on these ellipses, in whatever way the crystal is oriented, and indeed they appear in all cases. They come out very strongly in the photographs taken with copper sulphate crystals.

So far it has been assumed that the atoms of zinc and sulphur act in an identical manner with regard to the production of secondary waves, but this assumption is not necessary. What is brought
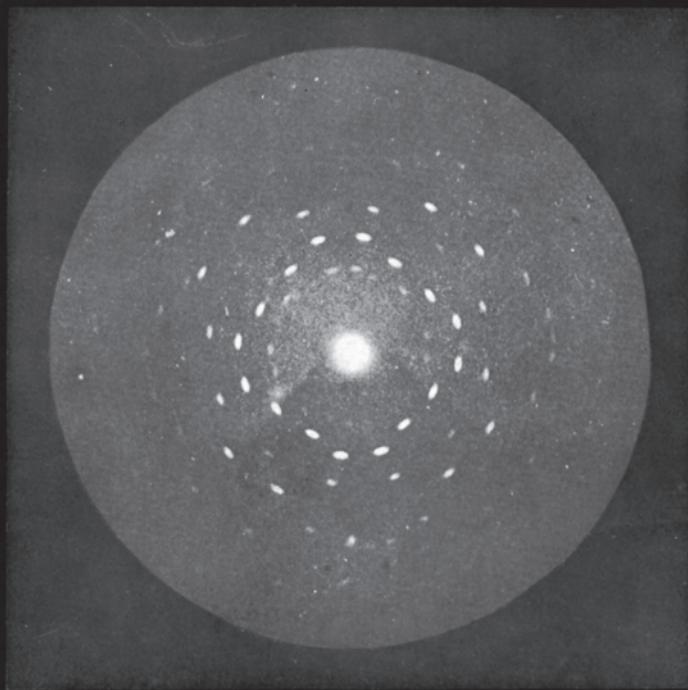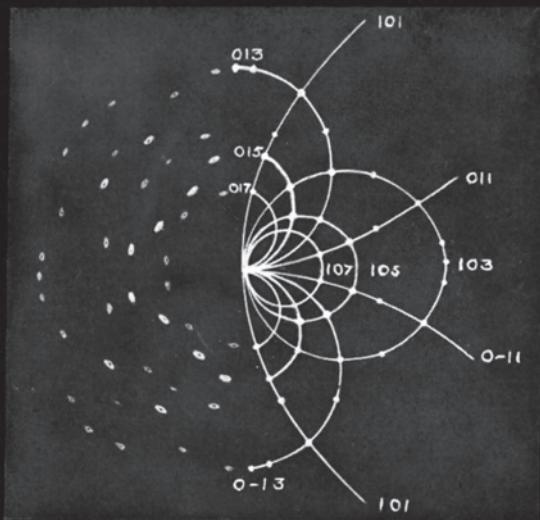
Fig. 3.

Fig. 4.

out so strongly by the analysis is this; that the point system to be considered has for element of its pattern a point at each corner of the cube and one at the centre of each cube face. In the arrangement assigned to cubical zinc sulphide and similar crystals by Pope and Barlow, this point system is characteristic of both the arrangement of the individual atoms regarded as equal spheres, and of the arrangement of atoms which are in every way identical as regards nature, orientation, and neighbours in the pattern. The atoms of zinc, for instance, in the zinc blende are grouped four together tetrahedron-wise, and as these little tetrahedra are all similarly oriented and are arranged themselves in the above point system, atoms of zinc identical in all respects will again be arranged in this point system. Which of these factors it is that decides the form of the interference pattern might be found by experiments with crystals in which the point system formed by the centres of all the atoms differs from that formed by the centres of identical atoms.

In conclusion, I wish to thank Professor Pope for his kind help and advice on the subject of crystal structure.

NOTES†

1. WLB begins with a brief description of the Laue experiment taken from the June 1912 publication.
2. Laue incorrectly assumes secondary X-ray waves emitted by molecules in the crystal would undergo interference to give rise to a diffraction pattern.
3. Laue, who knows little about crystals at this time, mistakenly places ZnS molecules at the corners of a cube.
4. By considering the X-rays to be scattered by individual molecules Laue derives a correct set of equations to describe the formation of the diffraction spots. Note that WLB makes a small mistake in equation (1): *ap* should be written as $a\beta$.
5. Laue mistakenly assumes that only a few wavelengths of X-rays are present in the incident beam#.
6. In particular he finds 5 wavelengths to partially explain his observed pattern of spots.
7. Here WLB disagrees, as he finds that with this assumption there are no spots that fully satisfy Laue's equations.
8. WLB suggests that the incident beam consists of a continuum of wavelengths, and implies that it is this reflected radiation that causes the spots, not fluorescent radiation from the atoms of the crystal. Laue argued in March 1913 that a continuum of X-ray wavelengths would give rise to a uniform darkening of the film, but Bragg's Law showed immediately why this is not the case.
9. Here WLB shows his mastery of optical physics, presumably referring to the book A. Schuster, *An Introduction to the Theory of Optics* (London: Arnold, 1909).
10. Instead of considering diffraction by each molecule, WLB proposes the breathtakingly simple model whereby X-rays can be thought of as being 'reflected' by planes of molecules or atoms, with the reflected rays interfering to produce either cancellation or reinforcement of intensity. It is because of this model that we now refer to the diffraction spots as *reflections*.
11. Here we see for the first time the appearance of *Bragg's Law*. In its initial form he chooses the angle θ to be the angle of incidence which gives the cosine form. In later work he changes this equation to be $\lambda = 2d \sin\theta$, the form that we all use today.
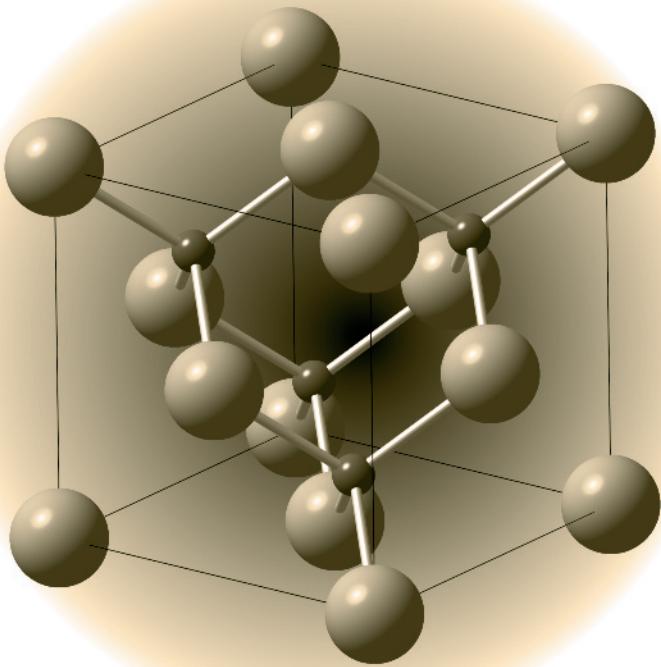
---

† WLB deliberately omitted "X-rays" from the title in in deference to his father who had until then advocated the corpuscular theory.

It is interesting to note that had Laue been correct in his assumption of a fixed wavelength then it is highly unlikely that Friedrich and Knipping would have observed any diffraction with their initial experiment, and so their great discovery would have been set back.

This shows that reflections occur only for particular combinations of d, λ and θ, thus giving rise to spots on a film rather than a uniform diffuse darkening. This very simple relationship is central to all modern analysis of crystal structures by X-rays, neutrons and electrons (and in many areas of modern optics), and is one of the most important equations in the history of science.

12. He points out that there is a relationship between the energy of the X-rays and the intensity of the spots.

13. WLB refers to the theories of Pope and Barlow who suggested that the structure of ZnS should be in the form of face-centred cubic arrays, rather than the model used by Laue. With this model WLB is able in the following paragraphs to explain why certain reflections are missing from Laue's pattern.

14. WLB starts by considering the structure of ZnS to consist of face-centred arrays.

15. A small error here: it should read 0 *a a.*

16. The discussion that follows is long and tortuous and uses geometric arguments to explain why this happens: remember that this was before the concept of structure factor formalisms came in to simplify such an analysis. At this stage WLB is unaware of the conventional use of Miller indices to denote crystal planes, something he corrects in subsequent publications.

17. He shows here that the spots fall on cones.

18. Here WLB indicates that his analysis is fundamentally the same as Laue's but his treatment is in a form that is more amenable to solving the crystal structure.

19. This where WLB explains that reflections are systematically absent when the indices that describe the planes are not all odd or all even, in precise agreement with Laue's pattern.

20. All other models of the ZnS structure do not fit Laue's pattern.

21. Evidence that the X-rays are scattered elastically by the crystal.

22. Tilting of the crystal changes the intensities of the spots dramatically, because of the change of wavelength.

23. The spot shape changes with distance from the crystal. This demonstrates that the spots cannot be explained by channelling of particles along 'avenues' in the crystal. Reflection of the incident circular beam is shown here to lead to focusing in the vertical direction but continued spreading in the horizontal direction, leading to elliptical spots, a noted characteristic of the initial Laue photograph. It is probably this observation that made WLB realise that it could be explained by reflection from crystal planes.

24. Up to this point WLB has not been specific about possible atomic arrangements, beyond showing that a cubic face-centred lattice explains the ZnS pattern. Here he points to tetrahedral arrangements of Zn atoms, and so he is suggesting at least a partial crystal structure determination. It is later in 1913 that he uses his father's ionization spectrometer (a fore-runner of the modern diffractometer), to complete his first <u>full</u> structure determination, in that case that of the alkali halides (*Proc. R. Soc. Lond. A* 1913 **89**, 248-277), followed by a paper with WHB on the structure of diamond (*Proc. R. Soc. Lond. A* 1913 **89**, 277-291).