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Centennial of X-ray diffraction: development of an unpromising experiment with a wrong explanation

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In February 1912 in Munich, P. P. Ewald, one of A. Sommerfeld's Ph.D. students, consulted M. Laue on matters related to crystal optics, his thesis subject. During the conversation, Laue conceived the idea that a crystal might act as a three-dimensional diffraction grating to the X-rays. Despite the idea having met with scepticism among his colleagues, Laue succeeded in getting the help of two of W. C. Roentgen's doctorands: F. Friedrich, Sommerfeld's laboratory assistant, and P. Knipping: to undertake the, by now, legendary experiments that originated a new branch of Physics. The results solved two fundamental questions of the time: namely are the X-rays electromagnetic radiation (light) of very short wavelength? And also, do the crystals have spatial periodic arrangements? The affirmative answer to both questions was immediately followed in 1913 by the instrumentation and re-interpretation of the phenomenon through the pioneering work by W. H. Bragg and his son W. L. Bragg, who paved the way to the portentous development of structural crystallography by X-ray diffraction that took place during the last hundred years.

Keywords: discovery of X-ray diffraction by crystals; Friedrich and Knipping's experimental proof; optical approach explanation: Laue's equation; W. L. Bragg's equation; W. H. Bragg's spectrometer; first crystal structure determinations

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1. Historical background

The turn of the nineteenth century was prolific in Physics discoveries and advances. At that time, among the several problems that attracted the scientist's interest, there was the answer to two (by then, uncorrelated) fundamental questions. An old one, namely are the crystals spatially periodic arrangements of matter? The other, a new one: are the recently discovered X-rays (W. C. Roentgen, 1895), particles?, as shown by the photoelectric effect produced by the rays; or electromagnetic (EM, light) waves?, as shown by the electrodynamics of its generation (G. G. Stokes, A. M. Liénard, E. Wiechert, independently in 1896), the polarization effects discovered by Barkla in 1906,[1] and the possible presence of diffraction effects from irradiated wedge-shaped pointed slits in the early experiments by Haga and Wind,[2] followed by experiments by Walter and Pohl,[3,4] whose more precise data were measured photometrically by Koch.[5] Sommerfeld applied the diffraction theory to explain these data, obtaining a rough estimate for the mean wavelength: $\lambda = 0.4 \text{ \AA}$ (0.04 nm).[6]

The notion that crystals consist of 'similar molecules similarly situated' goes back to the seventeenth century, well ahead of a detailed experimental verification. This picture, which Haüy (French mineralogist, 1743–1822) had elaborated at the end of the eighteenth century, was able to explain many empirical regularities of macroscopic crystals.[7,8] A lattice arrangement of point centres of force had been introduced by Seeber in 1824 [9,10] and had been assumed by A. L. Cauchy ca. 1830 in laying the foundations of elasticity theory. The mathematical theory of crystal lattices and their possible space groups was developed by J. F. C. Hessel (1830), M. L. Frankenheim (1835), and A. Bravais (1850); then extended by L. Sohncke in the 1870s and 1880s, and finally completed by A. M. Schoenflies, W. Barlow, and E. Fedorov ca. 1890 with the compilation of the full list of the 230 space groups in which a crystal lattice can be arranged in three dimensions.[11,12] This mathematical development can be summarized as follows: *The constituting atoms of stable crystals can be arranged in fourteen Bravais lattices, distributed in seven crystal systems according to the symmetry of a total of 230 space groups.*

In the 1900s, Germany was a world centre for the development of Physics and, particularly, Munich, gathered in three different laboratories not far from one another, a singular conjunction of capabilities well suited to answer the above two key questions, hence giving rise to a new branch of Science. In fact, the discoverer of X-rays, Wilhelm C. Roentgen, directed (from 1900) the Institute for Experimental Physics; Sommerfeld, who was researching on the nature of X-rays and their excitation by the stopping of cathode rays (electrons), was the Head of the Institute for Theoretical Physics, with Laue (a former Max Planck's disciple) as a staff member (from the fall 1909) specially interested in Optics, particularly diffraction Physics; and Paul H. Groth, the world's most famous authority on (pre-diffraction) crystallography was Director of the Institute for Mineralogy and Crystallography.

2. The seed

Towards the end of the summer semester of 1910, Ewald, a student of Sommerfeld, approached the Professor to ask for his supervision in a doctoral thesis. Sommerfeld presented to Ewald a list of some 10 or 12 topics to choose. Ewald picked up the last subject of the list, dealing with the theoretical derivation of the ‘optical properties of an anisotropic arrangement of isotropic resonators’. Sommerfeld had this problem last on his list because he had no definite idea on how to deal with it.[13]

3. The inspiration

Ewald had finished his calculations and was writing his thesis during the Christmas recess 1911 and in January 1912. To discuss some rather radical departures of his results from the traditional theory, Ewald sought the opinion of Laue, because of his strong knowledge of fundamental physical issues.[13] Previously, Laue had been commissioned by Sommerfeld (in 1911) to write a chapter on wave-optics in the Volume 5 of *Encyclopaedia of Mathematical Sciences* and was familiar with light diffraction by optical gratings.

In February 1912, Ewald met Laue to explain his work on optical waves in crystals. Laue could not help with the specific problem Ewald posed to him but rather asked: ‘what is the distance between the resonators?’ To this Ewald answered that it was very small compared to the wavelength of visible light, perhaps 1/500 or 1/1000 of the wavelength. In the course of the discussion, Laue asked what would happen if, instead of visible light, there were EM waves of very short wavelength propagating through the lattice? Ewald replied that this particular case could be dealt with within the framework of his theory, by just introducing an appropriate value of λ in the equations. In a momentous inspiration, Laue conceived the idea that *a crystal lattice could serve as an almost perfect three-dimensional diffraction grating for light with an extremely short wavelength, namely X-rays!*

4. The experimental proof

Like a seed in a fertile ground, Laue’s idea had developed in the right place and at the right time. However, Laue’s proposal to test experimentally his idea by bombarding a single-crystal with X-rays and look for diffraction maxima met with scepticism among many of his colleagues, including Sommerfeld and Wilhelm Wien themselves. The origin of this disbelief was in part due to a gross overestimation (by an order of magnitude) of the random displacement due to thermal motion of the atoms around their equilibrium positions in the crystal lattice. The faulty calculation amounted to a value of 0.75 Å for the atomic oscillation amplitude, close to the estimated values for X-ray wavelengths (Sommerfeld’s $\lambda = 0.4$ Å; Wien’s $\lambda = 0.7$ Å) and therefore large enough to destroy the degree of periodicity required for observing X-ray interference effects.[13] Despite the pessimism of his peers, Laue continued to discuss his idea and to seek for experimental help, even in the informal researchers’ gathering at the Café Lutz where prevailed the opinion that experiments were more reliable than theory and that, since the diffraction experiment required no elaborate set-up, it should be tried. Friedrich, a former Roentgen’s doctorate and now a Sommerfeld’s assistant (in charge of experiments on the generation of X-rays by stoppage of accelerated electrons in vacuum tubes) offered himself to do the work. After some initial opposition of Sommerfeld to divert the time of his assistant from his specific duty to an improbable experiment; and the joining to the team of Paul Knipping (who had just finished his thesis work at Roentgen’s Institute and was nicknamed ‘the watchmaker’ because of his experimental skills), Friedrich and Knipping started by Easter 1912 their ground-breaking and, by now, legendary experiments.

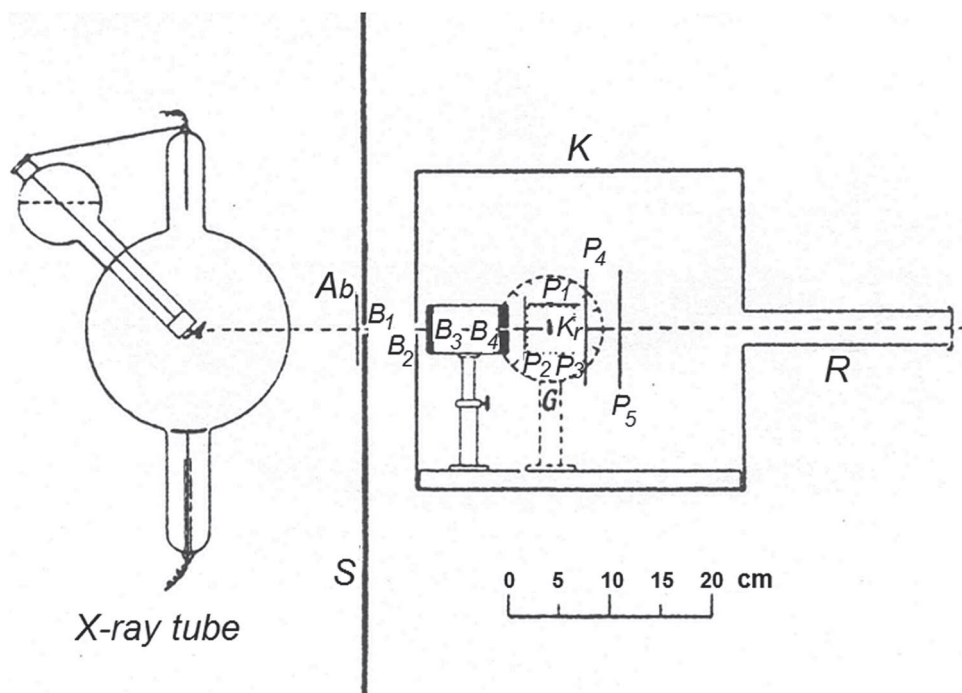


Figure 1. Experimental set-up employed by Friedrich and Knipping in their X-ray measurements. The source of Roentgen's radiation is separated from the crystal under investigation by a lead screen, *S*, pierced at B_1 , and a series of ever-finer lead diaphragms B_2 (in the lead chamber *K*), B_3 and B_4 . Around the crystal *Kr* photographic plates may be placed at various positions P_1 - P_5 . The extension *R* is added to trap the straightforwardly passing rays to avoid disturbing secondary rays due to the wall. For precision measurements, there is a diaphragm *Ab* for the pinhole B_1 in screen *S*. Figure adapted from Ref. [14] and reproduced with permission of John Wiley & Sons.

An improved version of the original experimental set-up is shown in Figure 1. The anticathode-crystal distance was about 35 cm. To avoid perturbing external effects, Friedrich constructed a lead box containing the crystal and the photographic plate; and initially collimated the X-ray beam by letting it pass through a 3 mm diameter hole drilled on the box side facing the tube (10 mm thick). A single-crystal of triclinic copper sulphate hydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) found in the laboratory was used as a target. It was positioned with no special orientation and fixed with wax to a holder within the box. The photographic plate was placed between the X-ray tube and the crystal on the assumption that the crystal would act like a reflection grating. The first exposure gave a negative outcome. Then, Friedrich and Knipping concluded that better results could be obtained by positioning the radiographic plate behind the crystal, as for a transmission grating. To cover the detection at wide scattering angles, Knipping insisted in placing plates all around the crystal.

The result of the second trial was positive. On the plate behind the crystal, surrounding the image of the incident X-ray beam, there appeared rings of blurred spots (Figure 2). Despite the picture fuzziness (in part due to the poorly collimated incident X-ray beam), it provided an unequivocal proof that some new property of X-rays had been found which had escaped all previous investigations (mainly dealing with transmission of the direct ray through matter), hence giving strong support to the correctness of Laue's idea of diffraction of X-rays by crystals.

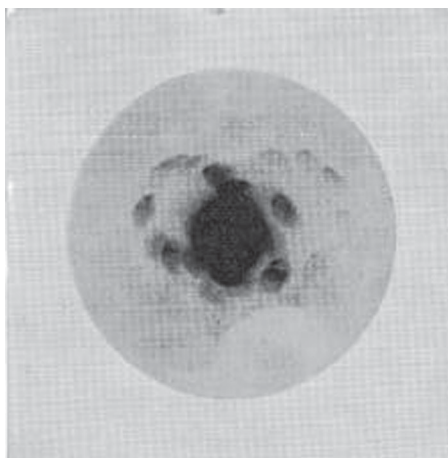


Figure 2. Friedrich and Knipping's first successful X-ray diffraction photograph of a copper sulphate single crystal, obtained after an exposure of 30 min. Reproduced from Ref. [14] with permission of John Wiley & Sons.

Laue learned the result at the Café Lutz and immediately went to the Institute to examine the data. According to Laue's recollections [15]:

I was plunged into deep thought as I walked home along Leopoldstrasse just after Friedrich showed me this picture. Not far from my own apartment at Bismarckstrasse 22, just in front of the house at Siegfriedstrasse 10, the idea for a mathematical explanation of the phenomenon came to me. Not long before I had written an article for the *Encyclopaedia of Mathematical Sciences* where I had to re-formulate Schwerd's theory of diffraction by an optical grating (1835), so that it would be valid, if iterated, also for a cross-grating. I needed only to write down the same condition a third time, corresponding to the triple periodicity of the space lattice, in order to explain the new discovery. In particular it was thus possible to relate the observed circular pattern of rays to the cones corresponding to the three interference conditions. The decisive day, however, was the one a few weeks later when I could test the theory with the help of another, clearer photograph.

Friedrich and Knipping pursued several experimental tests to make sure that the crystalline nature of the sample was involved in producing the pattern. To this purpose, they pulverized the crystal and kept the resulting powder in a little paper box while exposing it to X-rays. The photograph showed the central spot formed by the primary beam and the rings of large spots were absent. Only very small specks were seen in the region around the primary spot. They also had convinced themselves that only the primary spot was formed when the sample was removed altogether.

At this time, the three investigators themselves were wrongly convinced that the diffracted rays would consist of characteristic radiation emitted by the crystal under the influence of the incident X-ray beam. In fact, Friedrich and Knipping wrote in their paper:

a crystal had to be chosen containing a metal of considerable atomic weight, in order to obtain intense and homogeneous secondary rays, as these seemed the most suitable ones for the experiment. According to Barkla, metals of atomic weight between 50 and 100 were to be taken into consideration. Since initially we had no good crystal containing such metals, we used for the preliminary trials a fairly well-developed copper sulphate crystal.

Copper has atomic weight equal to 63.5; zinc, its neighbour in the Periodic Table, has an atomic weight of 65.4. It is therefore very likely that the above considerations prompted the purchase of high-quality zinc-blende plates as soon as the first results were obtained. Before these plates arrived, and during the period of construction of a more elaborate camera, diagrams

were taken with cleavage plates of cubic zinc-blende (ZnS), rock salt (NaCl), and galena (PbS). They confirmed the observations obtained with triclinic copper sulphate. The preliminary tests had included shifting the crystal parallel to itself, showing that all parts of the crystal gave the same pattern; fixing a second photographic plate behind the crystal at double the distance of the first one, on which a picture of double the size was obtained, hence proving that there were really secondary rays spreading out from the crystal; and finally, changing the orientation of the crystal by a few degrees to find that the position of the spots is very sensitive to the orientation of the crystal with respect to the incident X-rays. These last observations showed the convenience of constructing an improved apparatus so that not only the direction and delimitation of the incident ray, but also the orientation of the crystal, were accurately defined. The skilful Friedrich achieved this by setting up the crystal on a precise goniometer and using a collimating system consisting of a first hole of about 3 mm diameter in a 10 mm thick lead plate, followed at a distance of 70 mm by a much finer hole of 1.5 mm diameter, also drilled in 10 mm thick adjustable lead sheet. The experimental conditions during the more elaborate measurements of Friedrich and Knipping (cf. Figure 1) were as follows [14]:

Distance anticathode-crystal = 350 mm
Distance $B_3 - B_4 = 70$ mm (hole at B_3 of 3 mm in diameter)
Distance hole at B_4 -crystal = 50 mm (hole at B_4 of 1.5 mm)
Distance crystal-plates P1, P2, and P3 = 25 mm
Distance crystal-P4 = 35 mm
Distance crystal-P5 = 70 mm
Current in a moderately soft radiation tube = 2–10 mA
Exposition time = 1–20 h.

With the improved apparatus, the X-ray diffraction photographs were much better than the previous ones. Figure 3 shows one of Friedrich and Knipping's radiographic plates obtained with an oriented zinc-blende single-crystal.

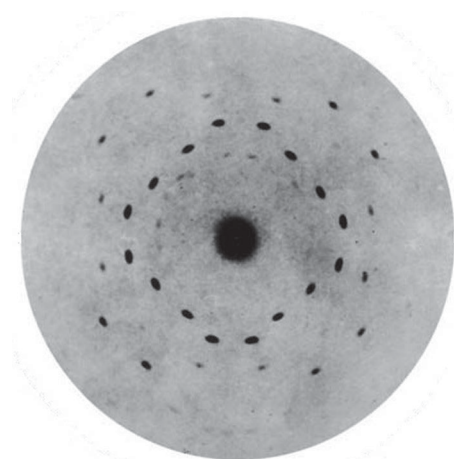


Figure 3. X-ray diffraction pattern of single crystal cubic zinc-blende obtained with the X-ray beam incident along the fourfold axis. Reproduced from Ref. [14] with permission of John Wiley & Sons.

5. The publication of the discovery

Laue, Friedrich, and Knipping's research was communicated to the Bavarian Academy of Sciences at the meetings of 8 June and 6 July 1912 by Sommerfeld as Fellow of the Academy. Roentgen seconded the acceptance and emphasized the relevance of the work. Two papers were published in the Proceedings of the Academy, one of them entitled 'Interferenz-Erscheinungen bei Röntgenstrahlen' ('Interference Phenomena with Roentgen Rays') by Friedrich et al.; [14] and the other one entitled 'Eine Quantitative Prüfung der Theorie für die Interferenzerscheinungen bei Röntgenstrahlen' ('A Quantitative Study of the Theory of Interference Phenomena in X-rays') by Laue. [16] Simultaneously with Sommerfeld's presentation in Munich, Laue himself reported on his discovery to his old group of Berlin physicists at the meeting of the Berlin Physical Society of 8 June 1912. Laue then went to Würzburg where he gave a seminar to Wien's Physics group. Erwin Madelung from Göttingen happened to be present and obtained from Laue the loan of his seminar slides to show them to his colleagues in Göttingen. The first of the papers published in the Bavarian-Academy contains 8½ pages under Laue's name, an introductory paragraph, and the theory of diffraction by a three-dimensional lattice. The remaining 11 pages are signed by Friedrich and Knipping and describe the preliminary and the final experimental results. Twelve Laue diagrams are reproduced by heliogravure on five plates. In the second paper, Laue applies the formulae of the general theory to a discussion of the ZnS diagram with X-rays incident along the crystal axis of fourfold symmetry.

We shall now review Laue's theoretical contribution employing modern mathematical notation. Laue considered a general triclinic crystal lattice of unit cell constants \vec{a}_j ($j = 1, 2, 3$) located at the origin of a coordinate system (Figure 4) of length N_j cells along each unit cell vector \vec{a}_j and having an atom of X-ray scattering amplitude f located at each lattice point, thus summing up a total of $N_1 \times N_2 \times N_3$ unit cells (or atoms).

The position $\vec{A}(l)$ of the atomic scatterers is given by

$$\vec{A}(l) = l_1 \vec{a}_1 + l_2 \vec{a}_2 + l_3 \vec{a}_3; \quad 0 \leq l_j \leq N_j - 1 \quad (j = 1, 2, 3). \quad (1)$$

If a monochromatic plane wave of X-rays with wave vector $\vec{k} = 2\pi \underline{k}$, $|\underline{k}| = 1/\lambda$: wave number is incident on the crystal, then the amplitude (electric field) of the elastic scattered wave of wave

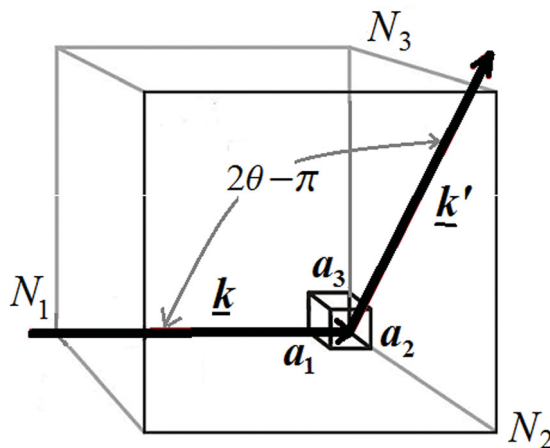


Figure 4. Diffraction from a tridimensional crystal lattice.

number \underline{k}' ($|\underline{k}'| = |\underline{k}|$) is given by

$$E = f(\Delta \underline{k}) \sum_{l_1=0}^{N_1-1} \sum_{l_2=0}^{N_2-1} \sum_{l_3=0}^{N_3-1} \exp[i2\pi \Delta \underline{k} \cdot \vec{A}(l)], \quad \text{with } \Delta \underline{k} = \underline{k}' - \underline{k}. \quad (2)$$

On account of Equation (1), the triple summation can be expressed as

$$F = \sum_{l_1=0}^{N_1-1} \exp[i2\pi l_1(\Delta \underline{k} \cdot \vec{a}_1)] \times \sum_{l_2=0}^{N_2-1} \exp[i2\pi l_2(\Delta \underline{k} \cdot \vec{a}_2)] \times \sum_{l_3=0}^{N_3-1} \exp[i2\pi l_3(\Delta \underline{k} \cdot \vec{a}_3)], \quad (3)$$

where each factor is a geometric series which can be readily summed up to give

$$\sum_{l_j=0}^{N_j-1} \exp[i2\pi l_j(\Delta \underline{k} \cdot \vec{a}_j)] = \frac{1 - \exp[i2\pi N_j(\Delta \underline{k} \cdot \vec{a}_j)]}{1 - \exp[i2\pi(\Delta \underline{k} \cdot \vec{a}_j)]},$$

and therefore

$$F = \prod_{j=1}^3 \frac{\exp[i2\pi N_j(\Delta \underline{k} \cdot \vec{a}_j)] - 1}{\exp[i2\pi(\Delta \underline{k} \cdot \vec{a}_j)] - 1} = \prod_{j=1}^3 \frac{\exp[i\pi N_j(\Delta \underline{k} \cdot \vec{a}_j)]}{\exp[i\pi(\Delta \underline{k} \cdot \vec{a}_j)]} \times \left[\frac{\sin \pi N_j(\Delta \underline{k} \cdot \vec{a}_j)}{\sin \pi(\Delta \underline{k} \cdot \vec{a}_j)} \right], \quad (4)$$

with corresponding diffraction intensity proportional to

$$I = f^2 \frac{\sin^2 \pi N_1(\Delta \underline{k} \cdot \vec{a}_1)}{\sin^2 \pi(\Delta \underline{k} \cdot \vec{a}_1)} \times \frac{\sin^2 \pi N_2(\Delta \underline{k} \cdot \vec{a}_2)}{\sin^2 \pi(\Delta \underline{k} \cdot \vec{a}_2)} \times \frac{\sin^2 \pi N_3(\Delta \underline{k} \cdot \vec{a}_3)}{\sin^2 \pi(\Delta \underline{k} \cdot \vec{a}_3)}. \quad (5)$$

For diffraction maxima, all three denominators must vanish, namely

$$\begin{aligned} \Delta \underline{k} \cdot \vec{a}_1 &= h, \\ \Delta \underline{k} \cdot \vec{a}_2 &= k, \\ \Delta \underline{k} \cdot \vec{a}_3 &= l, \end{aligned} \quad (6)$$

where h , k , l are integers.

As mentioned above, previously Laue had derived in *Encyclopaedia of Mathematical Sciences* the diffraction intensity of optical cross (2D) gratings involving the first two of the above factors in Equation (5) and the corresponding diffraction maxima given by the first two conditions in Equation (6). Now it was an easy matter for him to generalize the results to 3D gratings and X-ray light by adding the third factor in Equation (5) and the corresponding third maxima condition to Equation (6). *This was the mathematical explanation of the phenomenon that Laue imagined on his way home after seeing the first photograph that Friedrich showed to him.*

Laue's results can be cast in a more compact and revealing form. By expressing the wave vector change $\Delta \underline{k}$ as a function of its departure from a neighbouring reciprocal lattice vector \underline{H} ,

namely $\underline{K} = \underline{\Delta k} - \underline{H} \Rightarrow \underline{\Delta k} = \underline{K} + \underline{H}$, there results:

$$\sin^2 \pi N_j (\underline{\Delta k} \cdot \vec{a}_j) = \sin^2 (\pi N_j \underline{H} \cdot \vec{a}_j + \pi N_j \underline{K} \cdot \vec{a}_j) = \sin^2 (\pi N_j \underline{K} \cdot \vec{a}_j) \text{ and also:}$$

$$\sin^2 \pi (\underline{\Delta k} \cdot \vec{a}_j) = \sin^2 \pi (\underline{K} \cdot \vec{a}_j),$$

and the triple product of Equation (5) now adopts the expression:

$$\prod_{j=1}^3 \left[\frac{\sin^2 \pi N_j \underline{K} \cdot \vec{a}_j}{\sin^2 \pi \underline{K} \cdot \vec{a}_j} \right] = f_1(\underline{K}): \text{ Interference function,} \quad (7)$$

which for large N 's values adopts sharp maxima when $\underline{K} = 0$, namely $f_1(\underline{K} = 0) = (N_1 \times N_2 \times N_3)^2 = N^2$, with N = total number of lattice unit cells. Thus, the condition for 3D diffraction maxima is

$$\underline{\Delta k} = \underline{H}: \text{ Laue condition,} \quad (8)$$

one of the shortest and most meaningful equations in Physics.

In the second paper,[16] Laue applies his formulae of the general theory to discuss the ZnS diagram with X-rays incident along the crystal axis of fourfold symmetry (Figure 3). To describe the conceptual difficulties that his discussion faced, we must point out the ones dealing with the EM nature of the X-rays as was known at the time. In a vacuum tube, the X-rays are generated when an electron accelerated to kinetic energies of tens of keV is suddenly stopped by impact with an atom in the anticathode, hence emitting a short pulse of radiation whose width is of the order of magnitude of the atomic dimension. Moving at the speed of light, this implies an EM pulse duration of the order of 10^{-19} s. This view of X-rays as 'bremsstrahlung' has been put forward soon after Roentgen's discovery in 1895 and has been developed specially by Sommerfeld. From the inverse relationship between time duration τ and frequency bandwidth $\delta\omega$ of an EM pulse, namely $\tau \times \delta\omega \approx 1$ or in terms of energy $\tau \times \delta E \approx \hbar$, it turns out that the bremsstrahlung bandwidth is tens of keV and consequently the EM pulse has a very broad wavelength band. In addition, after 1907 the picture was complicated by the discovery that the bombarding electrons can also excite the emission from the anticathode heavy atoms of one or more characteristic, highly monochromatic, X-radiation (fluorescence). In fact, the time duration of this process is about 10^{-15} s and therefore the characteristic radiation has an energy spread of only about 1 eV and therefore a very sharp wavelength band (quasi-monochromatic radiation).

Laue's interpretation of the photos was mainly hampered by

- (i) A faulty extension from 1D and 2D diffraction gratings to what would be observed for 3D gratings. Laue believed that continuous (bremsstrahlung) radiation would not produce diffraction peaks but blackened photographic plates. However, the X-ray diffraction by a crystal is not a mere extension of an optical experiment from 2D to 3D gratings. In fact, an ingenious geometrical construction called Ewald's sphere,[17] involving the crystal 'reciprocal lattice', shows that a continuous and well-collimated X-ray beam scattered by a stationary crystal would consist in discrete spots due to (in general) different wavelengths. When the peaks were really observed, he found the interference maxima to be consistent with a set of five discrete wavelengths, but misinterpreted them as due to fluorescent lines from the crystal's heavier atoms excited by the primary X-ray beam, despite the prevailing belief that fluorescence emitted by crystal atoms is an incoherent process and therefore incapable of producing interference phenomena.
- (ii) His interpretation of the diffraction pattern for ZnS was additionally marred because he wrongly assumed a simple cubic (sc) lattice when in fact zinc-blende crystallizes in a face-centred cubic (fcc) lattice. This was made clear later by W. L. Bragg.

Max von Laue was honoured in 1914 with the Nobel Prize in Physics 'for his discovery of the diffraction of X-rays by crystals'.

6. The Braggs

In 1912 William Henry Bragg was a Cavendish Professor of Physics at the University of Leeds, to where he had moved in 1908 from Adelaide University, Australia. In Leeds he extended his previous study on ionization in gases by α -rays to X-rays, using in the latter case the anode characteristic radiation of vacuum tubes. He strongly favoured a corpuscular interpretation of X-rays because of the observed atomic photo-ionization effects excited by these rays.

Bragg's son, William Lawrence, was following in his father's footsteps pursuing a career in Physics. After an initial training in Physics and Mathematics in the University of Adelaide, he completed his education at the Cavendish Laboratory of Cambridge under J. J. Thomson, obtaining in 1911 his first appointment as lecturer at Trinity College.

News on Laue's discovery, including reproductions of Friedrich and Knipping's photographic plates, reached England and, particularly, W. H. Bragg. He interested his son in the finding and together they undertook an independent study of the subject, which started at Leeds during the summer of 1912. They initially tried the possibility of explaining Laue's patterns by some other assumption than that of the diffraction of waves. In fact, W. L. Bragg made some unsuccessful experiments to see if there was any evidence of 'X-ray corpuscles' moving along between rows of atoms in crystals.[18]

Seeing that the efforts to explain Laue's results in the framework of a corpuscular theory led to nowhere, W. L. Bragg commented in a 1943 account:

On returning to Cambridge to ponder over Laue's paper, however, I became convinced of the correctness of his deduction that the effect was one of wave diffraction, but also convinced that his analysis of the way it took place was not correct.

A clue as to the correct interpretation of the phenomenon was suggested by the following W. L. Bragg's observation on the shape of the diffraction spots on the radiographic plate (Figure 5):

When the plate was placed at P1 near the crystal the spots were almost circular like C1, but when placed farther back at P2 they became very elliptical (C2). Now Laue had ascribed his pattern to the diffraction of certain specific wave-lengths in the X-ray beam by the regular pattern of the crystal. Given a fixed wave-length, optical theory tells us that the diffraction must take place at a definite angle, and this means that the diffracted rays drawn in the picture should all have been parallel. I had heard J. J. Thomson lecture about Stokes' theory of the X-rays as very short pulses of electromagnetic radiation. I worked out that such pulses of no definite wave-length should not be diffracted only in certain directions, but should be reflected at any angles of incidence by the sheets of atoms in the crystal as if these sheets were mirrors. A glance at the geometry of the figure in which the rays are drawn as if reflected, shows that they close together again vertically while continuing to spread horizontally, thus explaining why the spots get more elliptical as the plate is placed farther away.

This observation led Bragg to interpret the X-ray diffraction pattern as due to the interference of reflected rays from the atoms located on families of parallel crystal planes. These planes would act towards X-rays similar to a parallel arrangement of equally spaced and semi-transparent mirrors towards incident light in Optics. Thus, the condition for constructive interference of reflected X-rays would be given by

$$2d \sin \vartheta = n\lambda : \text{Bragg's equation, where}$$

d = separation between closest planes in the family,

ϑ = glancing angle of the incident beam,

λ = X – ray wavelength,

n = reflection order.

(9)

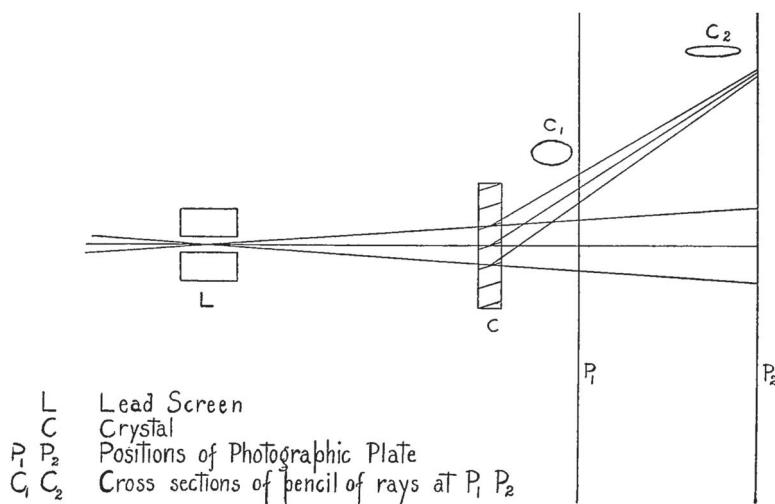


Figure 5. W. L. Bragg's interpretation of the shape of the spots on a Laue diagram as due to reflecting crystal planes. Reproduction of Figure 2 from Ref. [19]. Courtesy of Cambridge University Press.

Following a suggestion by Charles T. R. Wilson of trying a direct experiment of X-ray reflection from a crystal cleavage face, because such a face must be parallel to dense sheets of atoms, W. L. Bragg performed the experiment with mica, where he directed an X-ray beam on the cleavage surface of a 1 mm-thick mica slip at a glancing angle of 10° to find, after a few minutes of exposure, a well-marked reflected spot on a photographic plate located behind the slip. To further test that the reflection law was obeyed, Bragg (i) changed the incident angle and the slip-to-plate distance, (ii) bent the mica slip into an arc to observe that the reflected ray can be brought to a line focus.[20]

It remained to explain why certain of these atomic mirrors in the zinc-blende crystal reflected more powerfully than others, a difficulty which had led Laue to postulate a group of definite wave-lengths. William J. Pope and William Barlow had a theory that the atoms in cubic compounds like ZnS were packed together, not like balls at the corners of a stack of cubes, but in what is called cubic close-packing, where the balls are also at the centres of the cube faces (*fcc*). I tried whether this would explain the anomaly, and it did! It was clear that the arrangement of atoms in zinc-blende was of the face-centred type. I was careful to call my paper on the structure of zinc-blende "The Diffraction of Short Electromagnetic Waves by a Crystal" [19] because I was still unwilling to relinquish my father's view that the X-rays were particles; I thought they might possibly be particles accompanied by waves.

Though W. L. Bragg determined in this first work the correct Bravais lattice for ZnS (*fcc*), no detailed structure, however, of the compound was proposed.

7. The first crystal structure determinations

W. J. Pope, who was Professor of Chemistry at Cambridge, suggested to W. L. Bragg to apply his X-ray structural method to crystals of alkali halides, namely NaCl, KCl, KBr, and KI. It turned out that their Laue pictures, though still complex, were however simpler than those of zinc-blende and, after a laborious procedure, led Bragg to a complete solution of the structures. *These were the first crystals to be analysed by X-rays.*[21]

8. The X-ray spectrometer

In order to examine the reflected beam in detail, W. H. Bragg built an X-ray spectrometer. In this instrument, a crystal face can be set so as to reflect the X-rays at any angle, and the strength

of the reflected beam can be measured by an ionization chamber. With this instrument, W. H. Bragg made the next great discovery. In addition to the continuous (Bremsstrahlung) X-radiation with a wide spread of wavelengths (which W. L. Bragg had called 'X-ray pulses'), he found that each metal used in the X-ray tube as source of radiation gave a characteristic X-ray spectrum of definite wavelengths, just as elements give line spectra in the optical region.[22] With this work, W. H. Bragg laid the foundations of X-ray spectroscopy. The X-ray spectrometer (Figure 6) also proved to be a more powerful method of analysing crystal structure than the Laue photographs which W. L. Bragg had used initially, and indeed which W. L. Bragg argued was needed for him to be sure that his salt crystal structures from their X-ray Laue diagrams were certainly correct.

With this instrument, one could examine the various faces of a crystal in succession, and by observing the angles at which, and the intensity with which, they reflected the X-rays, one could deduce the way in which the atoms were arranged in the lattice. On the other hand, a suitable crystal face could be used to determine the wavelengths of the characteristic X-rays coming from different elements as sources. Thus, a monochromatic X-ray beam could be selected by reflection from a crystal (monochromator). W. H. Bragg measured the wavelengths

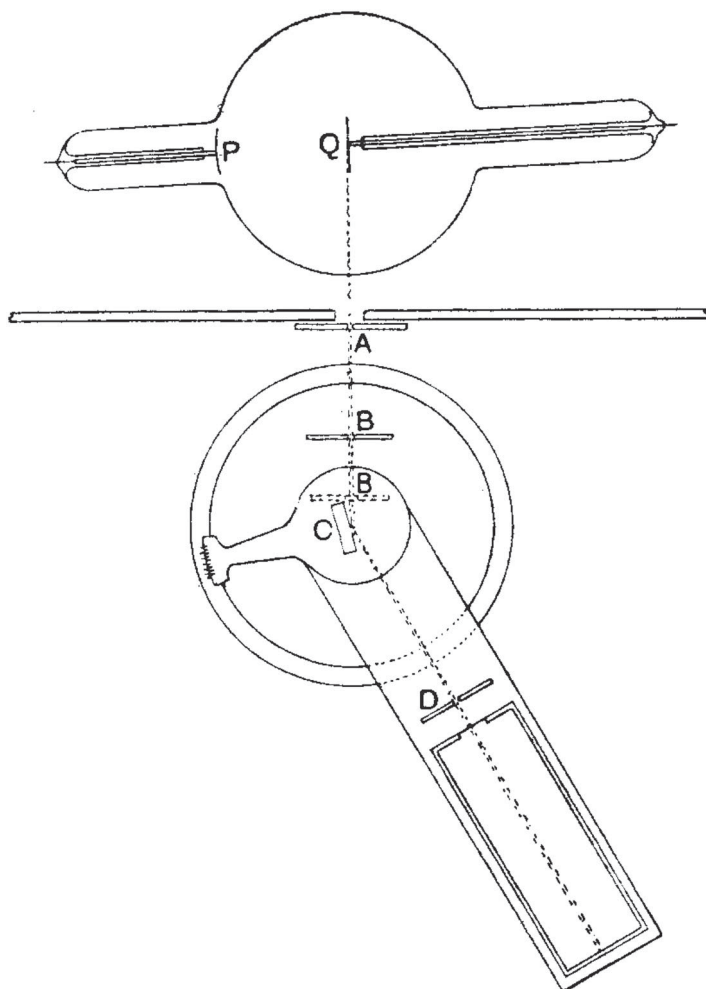


Figure 6. X-ray spectrometer. P, cathode; Q, anti-cathode; A, B, adjustable slits; C, crystal sample; D, slit; I, ionization chamber. Reproduction of Figure I from Ref. [22]. Courtesy of Nature.

of the X-ray spectra given by the elements platinum, osmium, iridium, palladium, rhodium, copper, and nickel. He identified them with Barkla's K and L radiations. He calculated their energy quanta according to Planck's relationship, and showed that this agreed with the energy of the cathode rays required to excite them. He showed that the shortest wavelengths ($K\alpha$ and $K\beta$) from various elements were similar, and that they were approximately inversely proportional to the square of the atomic weight. This first result anticipated the subsequent generalization of the principle by Henry G. J. Moseley, who used it to determine the atomic numbers. He also measured absorption edges, the critical wavelengths at which a sharp step in the absorption of X-rays by an element takes place.[23]

9. First analysis of crystal structures with the X-ray spectrometer

We shall review here W. L. Bragg's qualitative approach to the crystal structure determination for the series of alkali halides, based on considerations of crystal lattice symmetry, the atomic scattering strength (which he provisionally attributed to atomic weight A), the relative 'reflectivity' of the crystal planes based on the distribution of atoms that lay on them, and employing systematically his equation and a good deal of physical and chemical insight.[24] He showed that the diffraction data provided support to the proposed crystal model of Figure 7, consisting in two interpenetrating cubic fcc lattices, one of alkaline ions, the other with halide ions, relatively displaced to each other along a cell axis of half its length.

Bragg considered reflections in planes of atoms parallel to the three primary crystal planes (100), (110), and (111). For a simple cubic Bravais lattice (sc), the distances between neighbouring planes in each family are in the ratio $1 : 1/\sqrt{2} : 1/\sqrt{3}$ but no X-ray data of such a lattice were available at the time. However, Bragg noticed that this sc lattice (with half the cell constant of Figure 7) could be mimicked by potassium chloride (sylvine) because the X-rays will see almost identical scatterers as potassium and chloride are close to each other in the Periodic Table. In fact, he observed no diffracted intensity for the (111) reflection. He then

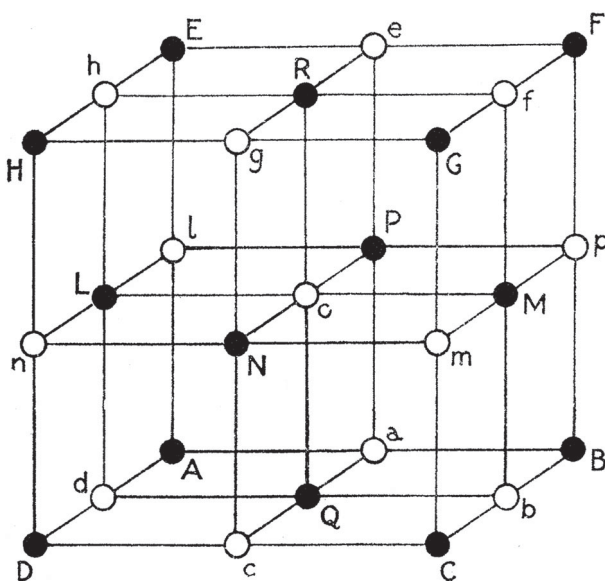


Figure 7. Rock-salt structure of alkali halides. Black disks indicate alkali (halide) ions and the open ones the halide (alkali) counter-ions. $AB = a$: cubic cell constant. Reproduction of part A of Figure 1 from Ref. [24]. Courtesy of the Royal Society.

measured reflection intensities from the (100) family of NaCl-containing planes, namely ABFE, dbfh, etc. in Figure 7, the (110) family of also NaCl-containing planes, namely BDHF, adhe, etc., and from the (111) family of intercalated Na-containing and Cl-containing planes, namely BDE (Na), adl (Cl), etc. The repetitive distance between planes in these families is in the ratios $1 : 1/\sqrt{2} : 2/\sqrt{3}$. He was then in possession of experimental X-ray diffraction data to validate the proposed cubic fcc Bravais lattice for the alkali halides series of salts. In fact, he could interpret the null (111) intensity in KCl as due to almost perfect cancellation effects of X-ray reflections from neighbouring BDE (K) and adl (Cl) planes in the lattice. Furthermore, the same consideration led him to interpret the weak intensity observed for the (111) line in NaCl, as now the reflection from the above planes, though in phase opposition, have different amplitudes because of the difference in scattering power of Na and Cl ions, hence leading to partial cancellation of the reflected waves. Similarly, Bragg interpreted the diffraction pattern of KBr and KI as mainly due to a single fcc of halide ions as these have an atomic scattering power much greater than their alkali counterpart.

Bragg was initially motivated in determining the X-ray wavelength from the diffraction pattern of the alkali halides. To this purpose, from his equation

$$2d(hkl) \sin \vartheta(hkl) = \lambda, \text{ where} \quad (10)$$

$$d(hkl) = \frac{a}{(h^2 + k^2 + l^2)^{1/2}},$$

and from the measured values of the diffraction angles $\vartheta(hkl)$ for the reflections in the above three families of planes, he found the values of the λ -independent ratios

$$\frac{a^3}{\lambda^3} = \frac{V}{\lambda^3}, \text{ where } V: \text{ unit cell volume.}$$

Bragg then calculated the cell volume V in an alternative way, based on the cubic fcc Bravais lattice he found for the alkali halides (which implies a number $Z = 4$ of molecules per unit cell), the molecular weight (MW), Avogadro's number (N_A), and the experimental density ρ of the solids, through:

$$\rho = \frac{Z \times \text{MW}}{V \times N_A}. \quad (11)$$

Bragg applied his procedure to the NaCl data to obtain $a = 5.6 \text{ \AA}$, and from Equation (10) the X-ray wavelength value $\lambda = 1.1 \text{ \AA}$, corresponding to the characteristic $L\beta$ emission line of the platinum anticathode of the X-ray tube he was using. *This is an important result:* (i) for the first time, a reliable absolute measure of X-ray wavelengths was possible, hence affording the quantitative determination of the geometry and metric of any crystal and their mutual comparison and (ii) the employment of monochromatic X-radiation (the one provided by the sharp characteristic lines of the anticathode element) affords a great simplification in the interpretation of diffraction patterns, as opposed to the cumbersome multi-wave Laue's method.

10. Crystal structure determination of diamond

W. H. Bragg was far more interested in the spectroscopy of X-rays than in crystals and most structure determinations were carried out by his son, with the only exception of a co-authored paper on diamond which showed the capability of the instrument he had devised.[25] In this work, the Braggs used an X-ray tube with an anticathode of rhodium because this metal gives a very strong and relatively monochromatic radiation consisting in one main characteristic radiation ($RhK\alpha$) of $\lambda = 0.607 \text{ \AA}$, and a much less intense monochromatic beam of $\lambda = 0.533 \text{ \AA}$ ($RhK\beta$)

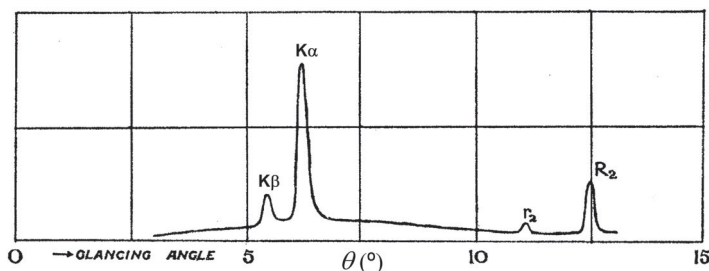


Figure 8. Spectrum of rhodium X-ray radiation, analysed through rock-salt 200 reflection. The r_2 and R_2 lines correspond to the 400 reflection of the characteristic $K\beta$ and $K\alpha$ lines. Adapted from Figure 1 of Ref. [25]. Courtesy of the Royal Society.

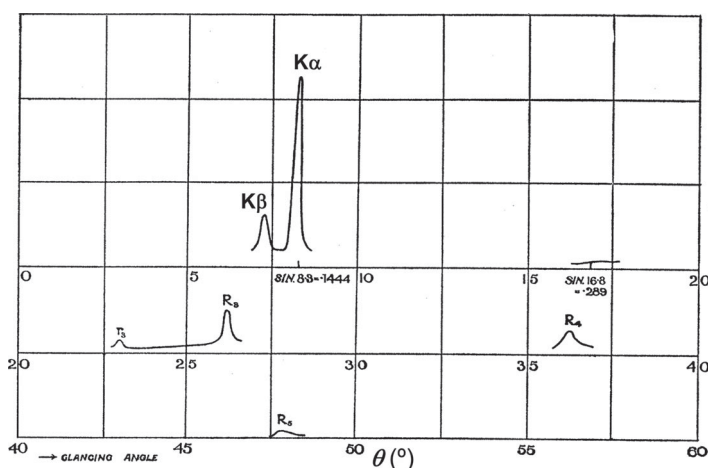


Figure 9. Diffraction spectra of rhodium X-rays reflecting from diamond (111) planes. Adapted from Figure 2 of Ref. [25]. Courtesy of the Royal Society.

and relatively little continuous radiation, as measured by the 200 reflection in an NaCl single-crystal acting as a monochromator (Figure 8). This is a very convenient feature to use with the ‘reflection (or Bragg’s) method’, which employs monochromatic radiation and to collect diffraction data with an ionization chamber. The other method is the original one called ‘Laue method’ that employs continuous radiation and the X-ray data are collected on photographic films.

Let us describe the essential steps of the procedure followed by the Braggs to unravel the crystal structure of diamond.

(1) They first measured the reflecting $\vartheta(hhh)$ angles from the first 111 to the fifth 555 reflection order from the natural cleavage (111) surface of a diamond employing rhodium X-radiation (Figure 9).

(2) From Bragg’s Equation (9)

$$2d(hhh) \sin \vartheta(hhh) = 2[d(111)/h] \sin \vartheta(hhh) = \lambda, \text{ where } d(111) = a/\sqrt{3},$$

they determined the common value of

$$\frac{\sin \vartheta(hhh)}{h} = \frac{\lambda}{2d(111)}, \text{ where } h = 1, 3, 4, 5$$

to be 0.1495, and from $\lambda = 0.607 \text{ \AA}$ the value of the inter-planar distance $d(111) = 2.03 \text{ \AA}$.

(3) Then, they assumed that diamond has a cubic fcc Bravais lattice (Figure 10), which hosts four lattice points per cell, and considered the distance between the members of the (100), (110), and (111) families of planes and their relative reflectivity:

- (i) The planes of atoms parallel to (100), as ABFE, RMQL, etc., are equally spaced in $a/2$ and contain equal numbers of scatterers.
- (ii) The planes of atoms parallel to (110), such as BDHF, are regularly spaced at a distance $a/2\sqrt{2}$ and also contain the same number of scatterers.
- (iii) The (111) planes, as EDB, HFC, are regularly spaced at a distance $a/\sqrt{3}$ and again are all equivalent to each other.

In what the Braggs called the ‘normal case’, any one of these sets of planes gives a series of diffraction spectra which diminish rapidly in intensity as we go from lower to higher orders. The relative diffraction line positions and qualitative intensities are shown in Figure 11. The Braggs considered the spectrum of (111) planes as a distinctive peculiarity of fcc lattices. In fact, if the effective centres were at the corners of an sc lattice of cell length a , then the spacing would be

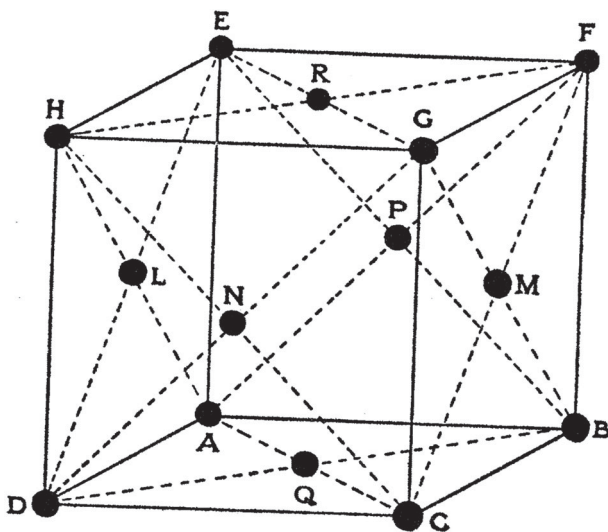


Figure 10. Cubic face-centred (fcc) Bravais lattice. Reproduction of Figure 3 from Ref. [25]. Courtesy of the Royal Society.

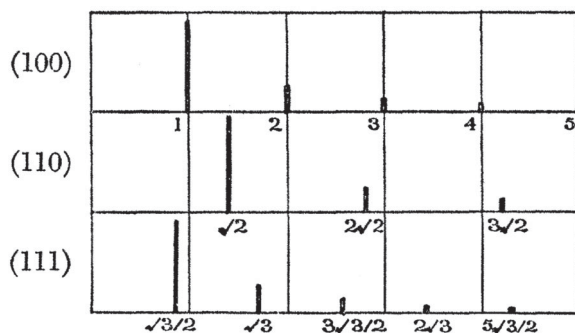


Figure 11. X-ray diffraction spectra of a cubic face-centred lattice. Reproduction of Figure 4 from Ref. [25]. Courtesy of the Royal Society.

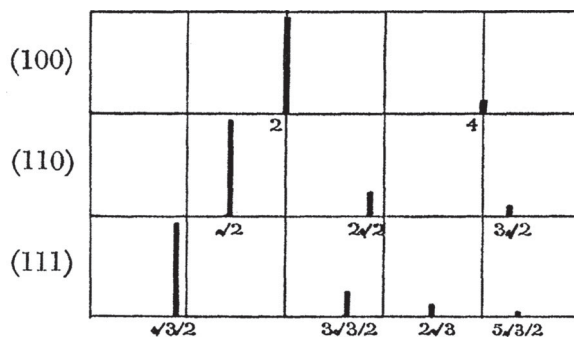


Figure 12. X-ray diffraction spectra of diamond. Reproduction of Figure 9 from Ref. [25]. Courtesy of the Royal Society.

a , $a/\sqrt{2}$, and $a/\sqrt{3}$, and the three sets of spectra would occur at $\sin \vartheta_{hkl}$ values proportional to the sequence (for the first three orders):

1, 2, 3; $\sqrt{2}$, $2\sqrt{2}$, $3\sqrt{2}$; $\sqrt{3}$, $2\sqrt{3}$, $3\sqrt{3}$, with the last set at variance with an fcc lattice, where the $\sin \vartheta_{hkl}$ ratios for (111) planes are in the sequence $\sqrt{3}/2$, $\sqrt{3}$, $3\sqrt{3}/2$.

(4) Now, they compared the fcc spectra of Figure 11 with individual cases to reveal their particular structures. For example, the peculiar NaCl (111) diffraction line can be described by the fact that the first-order spectrum is weak and the second-order strong. The interpretation is that the Na and Cl fcc sub-lattices are shifted from each other along the a -axis by half its length: the first-order 111 line tends to disappear and the second-order 222 to increase in importance. In the case of KCl, the K and Cl atoms scatter almost equally and then the 111 line disappears completely. In zinc-blende (ZnS) or iron pyrite (FeS₂), one kind of atom (the metal) is a much stronger scatterer than the other and therefore their spectra resemble the ones characteristic of mono-atomic fcc lattices.

(5) In the diamond case, the reflection orders on the (111) plane are shown in Figure 12. The Braggs first determined the number of carbon atoms per unit cell (Z) from their experimental value of the cell constant $a = \sqrt{3} d_{111} = \sqrt{3} \times 2.03 \text{ \AA} = 3.55 \text{ \AA}$, and the observed density ρ of diamond ($\rho = 3.51 \text{ g cm}^{-3}$) through Equation (11):

$$Z = \frac{\rho V N_A}{MW} = \frac{\rho a^3 N_A}{MW}, \text{ where}$$

$$MW = 12; \quad N_A = 6.023 \times 10^{23},$$

to obtain $Z \approx 8$ C-atoms per unit cell. The authors next locate an fcc sub-lattice with four C-atoms and noticed that the absence of the second-order reflection 222 implies that there must be another equivalent set of planes of atoms parallel to (111) planes that exactly bisect them. In fact, if successive reflections from neighbouring (111) planes are delayed in λ from each other and interfere constructively, then the successive reflections in (222) planes would lag in $\lambda/2$ and therefore interfere destructively.

Taking into account all the information, the Braggs made the simplest assumption fulfilling all data of locating the remaining four C-atoms on an fcc Bravais lattice shifted from the previous fcc lattice along the cube diagonal by $1/4$ of its length (Figure 13).

From the revealed diamond crystal structure, it turned out that each carbon is bonded to other 4 C-atoms in a perfect tetrahedral coordination with a bond length of $d(\text{C}-\text{C}) = \sqrt{3} a/2 = 1.522 \text{ \AA}$, a result that constitutes the *first direct experimental determination of a single C-C bond distance* of tetravalent sp^3 carbon.

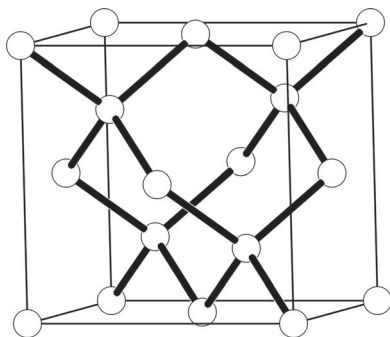


Figure 13. Unit cell content of diamond. The structure consists of two similar fcc lattices of C-atoms displaced from each other by a $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ translation along the cube diagonal. Drawn with ORTEP.[26]

The authors next compared the X-ray diffraction spectra of diamond with the one of zincblende to find that ZnS is built up in exactly the same way, except that the planes of atoms parallel to (111) now contain alternately either zinc or sulphur atoms only. This is evidenced by the reappearance of 200 and 222 lines in ZnS, which were absent in diamond as now the neighbouring (200) and (222) planes are interspaced by planes having different atomic species, namely Zn–S–Zn–S– and then the perfect destructive interference effect in diamond between C-containing planes is replaced by partial destructive interference due to Zn-containing and S-containing neighbouring planes in zinc-blende.

11. Exhaustion of early W. L. Bragg's method of 'trial and error'

By using single-crystal measurements with W. H. Bragg's X-ray spectrometer, many of the measurements also due to W. H. Bragg, W. L. Bragg was able to solve the crystal structures of zinc-blende (ZnS), fluorspar (CaF_2), cuprite (Cu_2O), iron pyrite (FeS_2), sodium nitrate (NaNO_3), and the calcite (CaCO_3) group of minerals.[24] ZnS and CaF_2 are the simplest because (as in the case of the alkali halides) the atoms occupy special positions in the crystal; FeS_2 and CaCO_3 are more difficult as the S and the carbonate ion are not fixed by symmetry and therefore to find their positions required a study more complicated (involving one or more adjustable structural parameters) than the ones the Braggs had carried on until then. As this work signals the limitations of the early W. L. Bragg's procedure of 'trial and error', let us review his determination of the iron pyrite structure, having only a single adjustable structural parameter.

- (1) Bragg used X-ray radiation from a palladium anode, which produces little continuous radiation and a large proportion of its spectral energy is concentrated in two lines ($K\alpha$ and $K\beta$), one ($K\alpha$) of wavelength $\lambda = 0.576 \text{ \AA}$, much stronger than the other one ($K\beta$).
- (2) Bragg measured the intensity for different angles with the ionization chamber. At all angles, there was a general (due to continuum X-rays) reflection. Then, he selected the ϑ -angles that satisfied the condition $2d \sin \vartheta = n\lambda$, with $\lambda = 0.576 \text{ \AA}$ and observed a strong special (due to the intense $\text{Cd}K\alpha$ line) reflection superposed on the general continuum. By subtracting the extrapolated intensity at neighbouring angles, he obtained the intensity of this special (monochromatic) reflection (Bragg had previously used rhodium rays which has a spectrum almost identical with that of palladium; Figure 8).
- (3) Bragg selected the first few orders of reflection on the same three primary planes as above, namely (100), (110), and (111) and measured the angular positions and intensities of the reflected beams from NaCl, CaF_2 , ZnS, and FeS_2 (Table 1) for comparison purposes.

Table 1. The angles give the setting of the ionization chamber and are twice the ϑ glancing angle.

Rock salt, Pd rays										
(100)	100	11.7°	30	23.8°	7	36.2°				
(110)	100	16.5°	24	34.0°	7	52.0°				
(111)	20	10.2°	100	20.6°	0	–	6	42.5°		
Fluor spar, Pd rays										
(100)	0	–	100	24.5°	0	–	13	50.5°		
(110)	100	17.4°	16	35.4°	6	51.5°				
(111)	100	10.7°	0	21.5°	10	32.5°	9	43.7°	3	53.5°
Zinc blende, Rh rays										
(100)	40	12.8°	100	25.9°	0					
(110)	100	18.2°	25	37.2°	7	57.5°				
(111)	100	11.4°	5	23.0°	8	34.7°				
Pyrites, Rh rays										
(100)	100	13.0°	0	26.2°	0	39.6°	14	53.8°	4	69.0°
(110)	100	18.1°	50	37.2°	0	–	0			
(111)	80	11.4°	100	22.6°	50	34.2°	0	–	22	58.8°

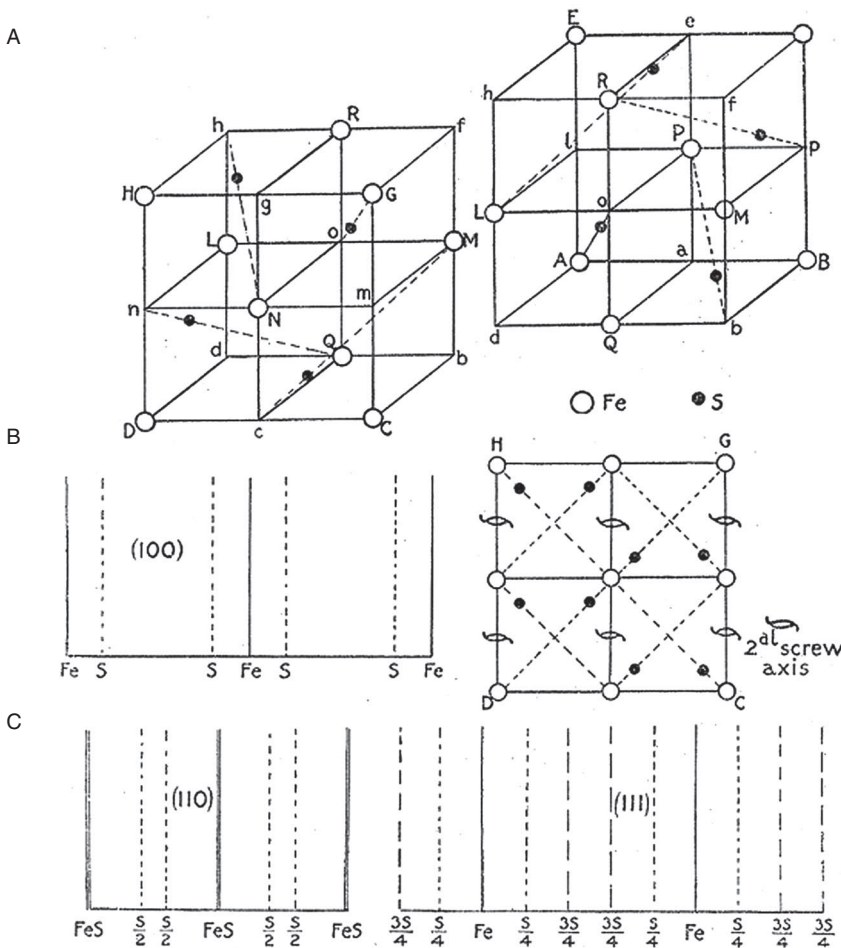
Notes: The numbers are proportional to the intensities of the spectra. Reproduction of Table I from Ref. [24]. Courtesy of the Royal Society.

- (4) Having determined that FeS_2 has a cubic fcc Bravais lattice with the Fe atoms at the cell corners and face centres, a first consideration suggested was for the sulphur atoms to take positions in the cell similar to the fluorine atoms in the highly symmetric structure of fluorspar (CaF_2), which Bragg had solved previously. Here, the Ca-atoms are also at the cubic fcc lattice points and twice as many fluorine atoms are at geometric centres of the eight sub-cubes into which can be divided the basic cubic unit cell (Figure 7). One thus could expect the X-ray diffraction spectrum of FeS_2 to resemble that of CaF_2 . As can be readily appreciated from Table 1, this is not the case and Bragg modelled the structure of FeS_2 by shifting the S-position from the sub-cubes body centres and along the cube diagonal to explain the observed X-ray spectra. This implies the introduction of a single variable parameter, namely the magnitude of the shift, to be determined from the X-ray data. To this purpose, Bragg followed the laborious procedure that is condensed in Figure 14.

To roughly estimate the diffraction intensities to be compared with the observed ones reported in Table 1, Bragg

- (i) assumed that one could apply to X-ray reflections from atomic crystal layers the analogous results on interfering reflections from multiple-layers in Optics;
- (ii) assumed as a ‘general law’ that ‘the diffracting power of an atom is proportional to the atomic weight’. In reality, it is roughly proportional to the atomic number Z ($Z \approx A/2$);
- (iii) identified the measured X-ray intensities as being proportional to the square of the resulting amplitudes;
- (iv) from empirical observations, assumed that the ‘normal’ spectra reflected from a simple series of identical (111) planes have intensities in the ratio 1, 0.2, 0.07, 0.03, and 0.01 for the first to fifth reflection orders.

W. H. Bragg and W. L. Bragg were jointly honoured in 1915 with the Nobel Prize in Physics ‘for their services in the analysis of crystal structure by means of X-rays’.



Therefore, we have the following comparison :

	Ratio.	Intensities.				
$I_{111}:I_{222}:I_{333}:I_{444}:I_{555}$ ratios	1 : 3	100	56	38	0	8
vs	1 : 4	78	100	35	2	21
d(Fe-S): sub-cube diagonal ratios	1 : 5	19	100	24	7	17
	Observed intensities.....	75	100	50	0	22

The 1 : 4 ratio seems, therefore, to be very nearly the true one.

Figure 14. Bragg's procedure to solve the structure of iron pyrite. Upper figure: (A) Front and rear half of the fcc structure of FeS_2 . (B) Projection of FeS_2 structure into the (100) face for d(Fe-S):sub-cube diagonal ratio equal to 1:5. (C) Crystal layers of Fe and/or S atoms as projected onto planes parallel to (100), (110), and (111) planes, indicating their content relative to iron. Reproduction of Figure 4 from Ref. [24]. Lower text: Analysis of the sulphur position by spectral analysis of $I(hhh)$ intensities. Comparisons of calculated and observed ratios of intensities (right) for the hhh reflections identified on the left. Similar comparisons were made for the $I(h00)$ and $I(hh0)$ spectral orders. Adapted from part of text on page 484 of Ref. [24]. Courtesy of the Royal Society.

12. Conclusions

For high symmetry crystals of simple compounds where atoms lay on lattice points, the ‘reflecting planes of atoms’ envisaged by Bragg resulted in a useful notion to solve the first structures. However, for even little more complicated crystals, the ‘reflecting plane’ concept becomes meaningless as the atoms in general are not arranged in such crystal planes, which are truly geometric, rather than physical objects. The concept of ‘reflecting planes’ was soon replaced by layers of modulated reflectivity which were represented by Fourier series, an advance anticipated by W. H. Bragg [23] and then elaborated by others.

Pretty soon it became clear that the light atomic electrons were the ones that scatter the X-rays; in fact the nuclei are too heavy to follow the rapid oscillations of this EM radiation (of about 10^{18} cycles per second).

For further progress in crystal structure determination, going beyond the early semi-quantitative methods of ‘trial and error’ mainly developed by the Braggs during the first half of the 1910s, there was the need for

- (1) a better description of the Physics behind the X-ray scattering by atoms, molecules, and solids including the atomic scattering factors of the atoms of different elements;
- (2) a detailed mathematical description of the diffraction of crystals (Fourier series);
- (3) general-purpose *ab-initio* resolution methods (Patterson, direct methods, anomalous dispersion-based methods, intrinsic phasing, etc.) to solve the so called ‘phase problem’ in crystallography;
- (4) improved and more powerful X-ray sources (Coolidge X-ray vacuum tubes, rotating anode, synchrotron radiation, the X-ray laser);
- (5) improved procedures of X-ray data collection (Weissenberg and precession cameras with photographic recording, automatic diffractometers equipped with scintillation counters, area detectors, etc.);
- (6) A substantial increase in computing power (development of electronic computers).

The advances in the solution of the above requirements produced during the last hundred years are at the core of modern structural crystallography.

Disclosure statement

No potential conflict of interest was reported by the author.

Notes on contributor



Oscar E. Piro received his Doctorate in Physics (Ph.D.) from the National University of La Plata (UNLP), Argentina, in 1977, in the field of Solid State Physics. He made post-doctoral research at the Department of Biophysics and Theoretical Biology of the University of Chicago, working on X-ray crystallography of biological macromolecules (1978–1980). He is one of the pioneers in the information theoretical approach (maximum entropy) to the solution of the ‘phase problem’. Upon his return to Argentina he became a Research Fellow of CONICET and currently he is Full Professor of UNLP. His research interest is grounded in Solid State Physics, particularly in Structural Crystallography by X-ray diffraction methods and also in the optical and spectroscopic (mainly infrared and Raman) properties of crystals. Currently, he works on the structure-physicochemical properties relationship of inorganic, organic, metal-organic (including minerals), bioorganic and bioinorganic, pharmaceutical (both natural and synthetic), and supra-molecular materials.

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