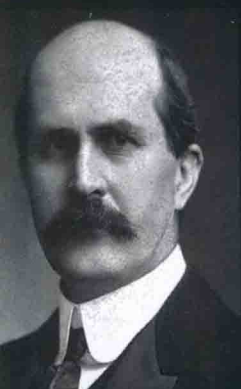


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# Early Days of X-ray Crystallography



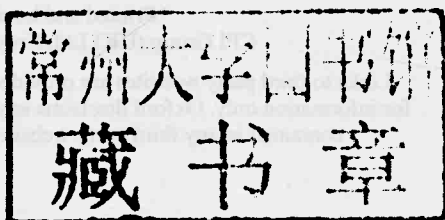
ANDRÉ AUTHIER



# Early Days of X-ray Crystallography

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## Dedication

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## PREFACE

The 2012 Nobel Prize for Chemistry was awarded to R. Lefkowitz and H. Hughes for studies related to the crystal structure determination of 'G-protein-coupled receptors', just one hundred years after one of the most significant discoveries of the early twentieth century, the discovery of X-ray diffraction by M. Laue, W. Friedrich, and P. Knipping (March 1912), and the birth of X-ray analysis (W. L. Bragg, November 1912). This award is the latest in a long list of Nobel Prizes awarded for work related to X-ray crystallography. Crystallography has come a very long way since the first crystal structure determinations by W. H. and W. L. Bragg, father and son, in the spring of 1913. The momentous impact of Laue's discovery in the fields of chemistry, physics, mineralogy, material science, biochemistry, and biotechnology has been recognized by the General Assembly of the United Nations by establishing 2014 as the International Year of Crystallography.

The immediate result of Friedrich, Knipping, and Laue's discovery was to confirm the wave nature of X-rays and the regular three-dimensional arrangement of atoms in crystals. It had two major consequences: the analysis of the structure of atoms, and the determination of the atomic structure of materials. The aim of this book is to give a fair account of the events surrounding the discovery itself. It relates the successive stages of the concept of space-lattice, from Kepler to Haüy, Schoenflies, and Fedorov, and the discussions about the nature of X-rays, wave or corpuscular. Within fifteen years or so of the discovery, the main bases of X-ray analysis were established, and our understanding of the nature of chemical bonds in solids had to be revised. The number of publications devoted to X-ray crystallography increased exponentially, and only the main results achieved during these first years are outlined in this book.

Historians of science have pointed out that, for a variety of reasons, the accounts by scientists as to how they reached a certain conclusion, or made a certain discovery, are not always reliable. A typical example in our story is that of R.-J. Haüy telling how the sight of a calcite crystal falling and breaking into small rhombohedra was at the origin of his investigations. This is how a legend was born, to be repeated later in every textbook. The tale of the discovery of X-ray diffraction by its discoverers has similarly been contested. As noted by Kragh (1987), scientists have a tendency to rationalize after the events in the light of later developments. An error also made sometimes in historical writings by scientists is to ascribe more recent concepts to ancient authors. Another point underlined by Whitaker (1979) is that scientists usually 'start from modern ideas and attempt to explain how they came about rather than trying to understand the approach of former generations, they rewrite history so that it fits in step by step with the physics'. This is sometimes called 'quasi-history', and I have done my best to avoid its pitfalls and anachronisms.

When considering a discovery, there are two possible approaches. The first, favoured by historians, is to view the discovery solely in the light of the knowledge of the time. The other, which is difficult to avoid, is to situate it within the framework of the development, usually not linear, of a scientific concept. It is indeed difficult for anyone writing about a given discovery

to ignore the advances that followed. Our present knowledge may even help us to make a critical analysis of the action of the discoverer and to understand, for instance, why a particular reasoning went wrong.

In writing this book, my aim has been simply to outline the successive steps that our understanding of the inner structure of crystals went through, and to tell the story of the early days of X-ray crystallography, putting the events into the context of their time.

André Authier

Peyrat-le-Château, October 2012

## ACKNOWLEDGEMENTS

This book would never have seen the light of day without the unfailing and constant help and support of Helmut Klapper. Not only did he read it critically as I was writing it, but he provided me with a great number of the earlier German texts which are not accessible via the Internet. I am greatly indebted to Jenny Glusker for her detailed remarks and useful suggestions on every chapter. I thank them both heartily. Francesco Abbona, John Edwards-Moss, Dieter Hoffmann, Shaul Katzir, Peter Paufler, and Marjorie Senechal read several chapters and sent me very useful comments, I am very grateful to them. I am also indebted to Francesco Abbona, Leonid Aslanov, Jean-Claude Boulliard, Vladimir Dmitrienko, Michael Eckert, Timothy Fawcett, Howard Flack, Hartmut Fuess, Hugo Heinemann, John Helliwell, Dieter Hoffmann, Thomas Kaemmel, Joseph Lajzerowicz, Anthony North, Yuji Ohashi, Peter Paufler, Bjørn Pedersen, and Ullrich Pietsch, who provided material or illustrations for the book.

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## SIGNIFICANCE OF THE DISCOVERY OF X-RAY DIFFRACTION

*The history of X-ray diffraction ranks as one of the epoch-making discoveries  
in the history of science.*

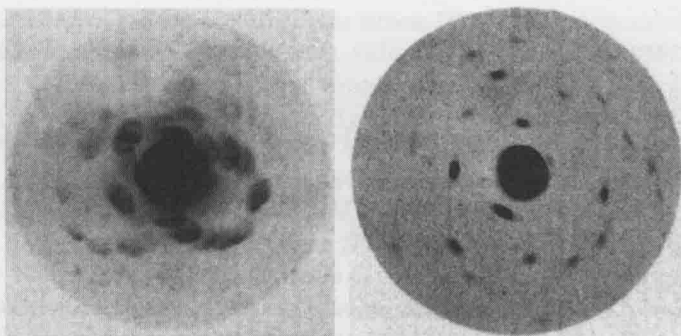
Sir W. H. Bragg and Sir W. L. Bragg (1937)

### 1.1 April 1912: a major discovery

April 1912. Munich, Institute for Theoretical Physics. The photographic plate, developed after a few hours of exposure, 'betrayed the presence of a considerable number of deflected rays, together with a trace of the primary ray coming directly from the anticathode' (Laue, Nobel lecture, 12 November 1915). This was the first photograph to show the diffraction of X-rays by a crystal. In this preliminary experiment, a crystal of copper sulphate pentahydrate was put in the X-ray beam with a natural face roughly normal to it, but otherwise arbitrarily oriented. This particular crystal was chosen because of its good shape, and also because it contained copper and it was thought that the expected result 'would have something to do with fluorescence' (Friedrich *et al.* 1912). Fig. 1.1, *Left*, shows the very first X-ray diffraction photograph, with rather diffuse spots and Fig. 1.1, *Right*, one of the next pictures, with narrower slits for the beam to pass through, and exhibiting much sharper spots. The story of the discovery is told in Chapter 6. Its importance was immediately felt by the three participants: the conceiver of the experiment, Max Laue, and the two experimentalists, Walter Friedrich and Paul Knipping, as well as by the circle of A. Sommerfeld's and W. C. Röntgen's co-workers meeting regularly at the Café Lutz in Munich. The feeling of excitement spread very rapidly to their contemporaries in Germany and abroad (see Section 6.7).

The significance of the discovery was two-fold.

1. *Firstly*, it might throw some light on the nature of X-rays: are they electromagnetic waves or corpuscles? This point had been debated hotly since the discovery of X-rays by W. C. Röntgen in 1895 and is the topic of Chapter 5. As early as 1896, O. Lodge (1896c), G. G. Stokes (Stokes 1896a, b), and E. Wiechert (1896a, b) had put forward the hypothesis that Röntgen rays were electromagnetic waves. The same suggestion was made by J. J. Thomson (1898a). C. G. Barkla had discovered the polarization of X-rays in 1904 (Barkla 1905a, b). H. Haga and C. H. Wind (1903) and B. Walter and R. Pohl (1908, 1909) had observed the diffraction of X-rays by a slit (see Section 5.9). Their experiments, controversial as they were, led to estimates of the X-ray wavelengths by A. Sommerfeld (1912). Another evaluation was made by W. Wien (1907) who, generalizing Planck's theory of light quanta, reckoned that the maximum energy transferred by X-rays to secondary electrons of velocity  $v$  and mass  $m$  is  $(1/2)mv^2 = hc/\lambda$  ( $h$  Planck constant,  $c$  velocity of light,  $\lambda$  X-ray wavelength), and deduced the X-ray wavelength from the measurement of the velocities of the electrons. Independently, J. Stark (1907), also using Planck's relation, deduced the energy of the light quanta from the energy of the primary electrons accelerated through a potential  $V$  (see Section 5.10).



**Fig. 1.1** *Left:* very first picture of a copper sulphate crystal. *Right:* new picture obtained with narrower slits. After Friedrich, Knipping, and Laue (1912).

On the other hand, William Henry Bragg in England was a staunch defender of the corpuscular theory. He held the view that the X-rays were material in nature, rather than æther pulses, and consisted of neutral pairs, such as pairs consisting of one  $\alpha$  or positive particle and one  $\beta$  or negative particle (W. H. Bragg 1907; Bragg and Madsen 1908*a, b*, see Section 5.8). The fact that the ionization observed in an ionization chamber was clearly due to electrons produced by the X-rays and not by the X-rays themselves was considered to point to the corpuscular nature of X-rays. Stark (1909*a, b*) was led to the same conclusion by the photoelectric effect. W. H. Bragg's reaction to Laue's experiment was reserved (W. H. Bragg 1912*a*, see Section 6.10): he saw 'some remarkable effects', and 'a curious arrangement of spots some of them so far removed from the central spot that they must be ascribed to rays which make large angles with the original pencil'. He concluded that 'it is difficult to distinguish between various explanations which suggest themselves. It is clear, however, that the diagram is an illustration of the arrangement of the atoms in the crystal'. He added that, as his son (William Lawrence Bragg) pointed out to him, the directions of the secondary rays follow 'avenues' between the crystal atoms, a view also held by J. Stark (1912, see Section 6.9). This interpretation was in line with the interpretation of X-rays as corpuscles. Lawrence Bragg was soon to change his own attitude, however, after some unsuccessful experimental attempts (Ewald 1962*b*), and, in a paper read to the Cambridge Philosophical Society on 11 November 1912, he explained Laue's experiment by the reflection of electromagnetic waves in a set of lattice planes (W. L. Bragg 1913*a*, see Section 6.11). His father wondered whether the effects observed were due to the X-ray themselves or to electromagnetic radiation associated with corpuscular rays (W. H. and W. L. Bragg 1937), but he came round reluctantly (W. H. Bragg 1912*b*), insisting that 'the properties of X-rays point clearly to a quasi-corpuscular theory'. 'The problem', he added, is not 'to decide between the two theories, but to find one theory which possesses the capacities of both'. It is only after the discovery of the Compton effect (Compton 1923*b*, see Section 9.5) and the formulation by L. de Broglie of the relations between the properties of light and those of the atom that the dual nature, corpuscular and wave, of X-rays was really understood.

Lawrence Bragg (1912), at the suggestion of his former optics teacher, C. T. R. Wilson,<sup>1</sup> quickly checked his explanation of the diffraction of X-rays by crystals by observing on a

<sup>1</sup>Charles Thomson Rees Wilson, born 14 February 1869 in Scotland, died 15 November 1959 in Scotland, was a British physicist and meteorologist who received the physics Nobel Prize in 1927 for his invention of the cloud chamber.

photographic plate the reflection of X-rays by a sheet of mica, while his father recorded it with an ionization chamber (W. H. Bragg 1913a). Recording the diffracted intensities with the ionization chamber proved in the future to be a much more powerful means for examining crystal structures than Laue photographs.

2. *Secondly*, the discovery confirmed the space-lattice hypothesis. At the beginning of August 1912, the English crystallographer A. E. H. Tutton<sup>2</sup> visited Paul von Groth, Director of the Institute of Mineralogy in Munich, and Max Laue, at Arnold Sommerfeld's Institute of Theoretical Physics. In his account of the visit, published in *Nature* under the title *The crystal space lattice revealed by Röntgen rays* (Tutton 1912b, 14 November), Tutton reported that Groth and Laue had showed him 'extraordinary' photographs obtained a few months before by W. Friedrich and P. Knipping, and had expressed the opinion that they formed 'an interference (diffraction) photograph of the Bravais space lattice'. He concluded that 'they do in reality afford a visual proof of the modern theory of crystal structures built up by the combined labours of Bravais, Schoenflies, Fedorov, and Barlow. Moreover, they emphasize in a remarkable manner the importance of the space lattice'. He added that, in his opinion, Friedrich and Knipping's photographs 'may form a crucial test of the accuracy of the two rival theories, now being discussed as to the nature of X-rays, the corpuscular and the wave theory'.

In his Becquerel Memorial Lecture to the Chemical Society on 17 October 1912, Sir Oliver Lodge<sup>3</sup> commented (Lodge 1912): 'This, if it be a fact, will have to be recognized as a striking and admirable case of scientific production, the various crystalline structures and accuracy of characteristic facets having been indicated by theory long before there was any hope of actually seeing them; so that once more—always assuming that the heralded discovery is substantiated—the theoretical abstraction will have become concrete and visible'.

Ewald, in the accounts he gave much later of the discovery of X-ray diffraction (Ewald 1932, 1962a and b), wrote that the concept of space lattice was then discredited, on one hand because the Cauchy relations between elastic constants, derived assuming a space lattice, were not verified by experiment, and on the other hand because there was no physical property which could be related to it. This position was strongly contested by the historian of science, P. Forman (1969), who accused Laue and Ewald of having created a myth out of the discovery of X-ray diffraction (see Section 6.12). Section 1.2 describes the views of the crystallographers of the time concerning the space-lattice concept. The problem of the validity of the Cauchy relations is discussed in Section 2.3.

He started work on the cloud chamber in 1895 in the Cavendish Laboratory in Cambridge and observed in early 1896 the 'rain-like' condensation after exposure to the newly discovered X-rays. In 1911, he was the first to observe the tracks of individual alpha- and beta-particles and electrons, confirming W. H. Bragg's predictions. He was lecturer and demonstrator at the Cavendish Laboratory at the time of W. L. Bragg's first experiments. He was awarded the 1927 Nobel Prize for Physics, 'for his method of making the paths of electrically charged particles visible by condensation of vapour'; the prize was divided between him and A. H. Compton.

<sup>2</sup>Alfred Edwin Howard Tutton, born 22 August 1864 in England, died 14 July 1938 in England, educated at the Royal College of Science in London, was an English crystallographer. He was a lecturer and instructor in chemistry and, at the same time, inspector of Technical Schools in London, Oxford, and Devon successively. All his life was devoted to precise measurements of crystals of several series of isomorphous salts, such as sulphates, selenates and their double salts.

<sup>3</sup>Sir Oliver Lodge, born 12 June 1851 in England, died 22 August 1940 in England, was an English physicist. He obtained his BSc degree and his DSc from the University of London. After being Professor of Physics and Mathematics at University College, Liverpool, he became in 1900 the first principal of the new Birmingham University, remaining there until his retirement in 1919. He elaborated on Maxwell's aether theory and is well known for his work on electrolysis, electromagnetic waves, and wireless telegraphy.

Both M. Laue's interpretation of the diagrams by means of the Laue equations (Friedrich *et al.* 1912) and W. L. Bragg's with Bragg's law (W. L. Bragg 1913*a*) established a fundamental relationship between X-ray wavelengths and the parameters of the crystal lattice. This had two major impacts for the future development of the science:

1. *Atomic structure of materials*: Knowing the X-ray wavelength, one can determine the lattice parameters of crystals; more generally, the analysis of the X-ray diagrams leads to the determination of the arrangement of atoms in materials. This 'became one of the powerful weapons of modern science, of which it has affected nearly every branch', in the words of Sir W. L. Bragg (1959), as will be outlined in Section 1.3. The first steps of crystal structure determination will be described in Chapter 8.
2. *Structure of atoms*: Conversely, knowing the lattice parameter of a crystal, one could determine X-ray wavelengths. Measurements with W. H. Bragg's ionization spectrometer showed that the spectrum contained both a continuous spectrum of 'Bremstrahlung' pulses and characteristic wavelengths, which corresponded to those discovered by Barkla (1906*b*). The relations between the wavelengths of the emission spectra determined by means of X-ray diffraction and Barkla's absorption spectra were generalized by H. G. J. Moseley (1913, 1914) who assigned atomic numbers to the elements (see Section 7.8). Moseley's pioneer investigations formed the starting point for the experimental researches on X-ray spectra, in particular by the Siegbahn group, and the theories about the structure of the atom by Kossel, Sommerfeld, Pauli, and others. The need for improvements in the theory followed the increase in the accuracy of the measurements of X-ray frequencies, and these measurements 'were and remain the most direct and accurate method to determine the energy levels of the atoms' (Cauchois 1964). The early stages of the development of X-ray spectroscopy are briefly recalled in Section 10.6.

## 1.2 Crystallography on the eve of the discovery of X-ray diffraction

The concept of space lattice (point-systems) introduced by Bravais (1848) was the result of a long process (see Chapters 11 and 12). It was generally accepted by crystallographers in the beginnings of the twentieth century, and it was also known by many chemists, for instance, by the American physical chemist Harry Clary Jones (1865–1916) who wrote in his *Elements of physical chemistry* (Jones 1903): 'In crystals the particles are arranged in a perfectly orderly manner, and fulfil the condition that the arrangement about one point is the same as about any other point'. Modern theories were described in several writings. Tutton's book (Tutton 1911) had presented a simplified approach, and Hilton (1903) had made a synthesis in English of Fedorov's, Schoenflies', and Barlow's formal derivations of the 230 groups. The definition of a crystal had evolved, from Haüy's simple one, that 'every crystal has a regular shape and its faces can be represented by a geometrical figure', to the sophisticated definition given by P. Groth in a lecture to the British Association for the Advancement of Science during a meeting held in Cambridge on 19 August 1904: 'A crystal—considered as indefinitely extended—consists of interpenetrating regular point systems, each of which is formed from similar atoms; each of those point systems is built up from interpenetrating space lattices, each of the latter being formed from similar atoms occupying parallel positions. All the space lattices of the combined system are geometrically identical and characterized by the same elementary parallelepiped' (Groth 1904).

Haüy and those who followed him had implicitly assumed that crystals are what we would call now 'molecular crystals', namely crystals where there are recognizable molecules in the structure, linked by weak forces. Groth (1888) made a very thorough discussion, based on considerations about dimorphism and isomorphism, on what could be the nature of the chemical molecule in the crystal. But, what with Barlow's work on close-packed structures (see Section 12.13) and the recent theories of crystal structure involving the repetition of elemental domains (*Fundamentaltbereiche*, Schoenflies 1891) by the symmetry operations of the space groups (see Section 12.14), new ideas began to appear as to the possible nature of the crystal molecules. In his 1904 lecture, Groth noted that, while molecules in an amorphous substance represent individual entities, in crystals they are assemblages of atoms belonging to different point systems. For instance, in sodium chloride, one cannot tell to which particular sodium atom a chlorine atom is linked, a view which, at the time, was not accepted by all chemists (see Section 10.1.1). This idea was proposed by W. Barlow and H. Pope (see Section 12.13), but was still found to be 'more than repugnant to the common sense, not chemical cricket' by the influential chemist H. E. Armstrong (1927), fourteen years after W. L. Bragg (1913*b*) had determined the structure!

Some people, however, considered the derivation of the 230 space groups as a purely mathematical theory, not as a physical one. They criticized the fact that the theory did not make any hypothesis as to the nature of the content of the repeating units, and felt that it did not add anything to the principle of the triple periodicity of crystals (Friedel 1907). The well-known specialist of crystal physics, W. Voigt, a student of F. E. Neumann, wrote in 1910 that the works of Schoenflies and Fedorov are predominantly mathematical in nature and that 'it is too early to judge their physical value' (Voigt 1910). Ewald (1962*b*) was correct in saying that 'no physicist, no crystallographer was able to assign correctly to a given crystal one, or even a small selection, of the 230 possibilities of arrangement which this theory predicted, and it was left wide open for discussion what was the nature of the particles that were arranged in the three-dimensionally periodic fashions which the theory allowed'. The situation changed of course radically after the discovery of X-ray diffraction. It was soon to appear that the only way to interpret the diffraction diagram of a crystal and to describe its structure was by reference to the space group to which it belongs (Niggli 1919).

The only crystallographic information that was available to mineralogists and chemists came, as in Haüy's time, from the observation of the crystal habit and the cleavage planes, and from the accurate measurement of angles. A great amount of data was gathered, but the general consensus was that, to have any hint about the structure, this information should be combined with the best knowledge possible of all the other properties (Groth 1904; Friedel 1907). It was generally agreed that the characteristics of the elemental parallelepiped of the lattice should be determined from the most important faces of the crystal, chosen according to their occurrence and their extent. They correspond to the planes of highest reticular density (Fedorov 1902, 1912; Groth 1904; Friedel 1907), and this is nothing else but the Bravais law, which states that the cleavage planes are the planes with the highest interplanar distance (see Section 12.11.3), and which had remained unnoticed for fifty years. Friedel (1907) and Fedorov (1902, 1912) pointed out that the order of the most important faces observed does not always coincide with the theoretical order because some faces may be missing, in particular in merohedral crystals. More