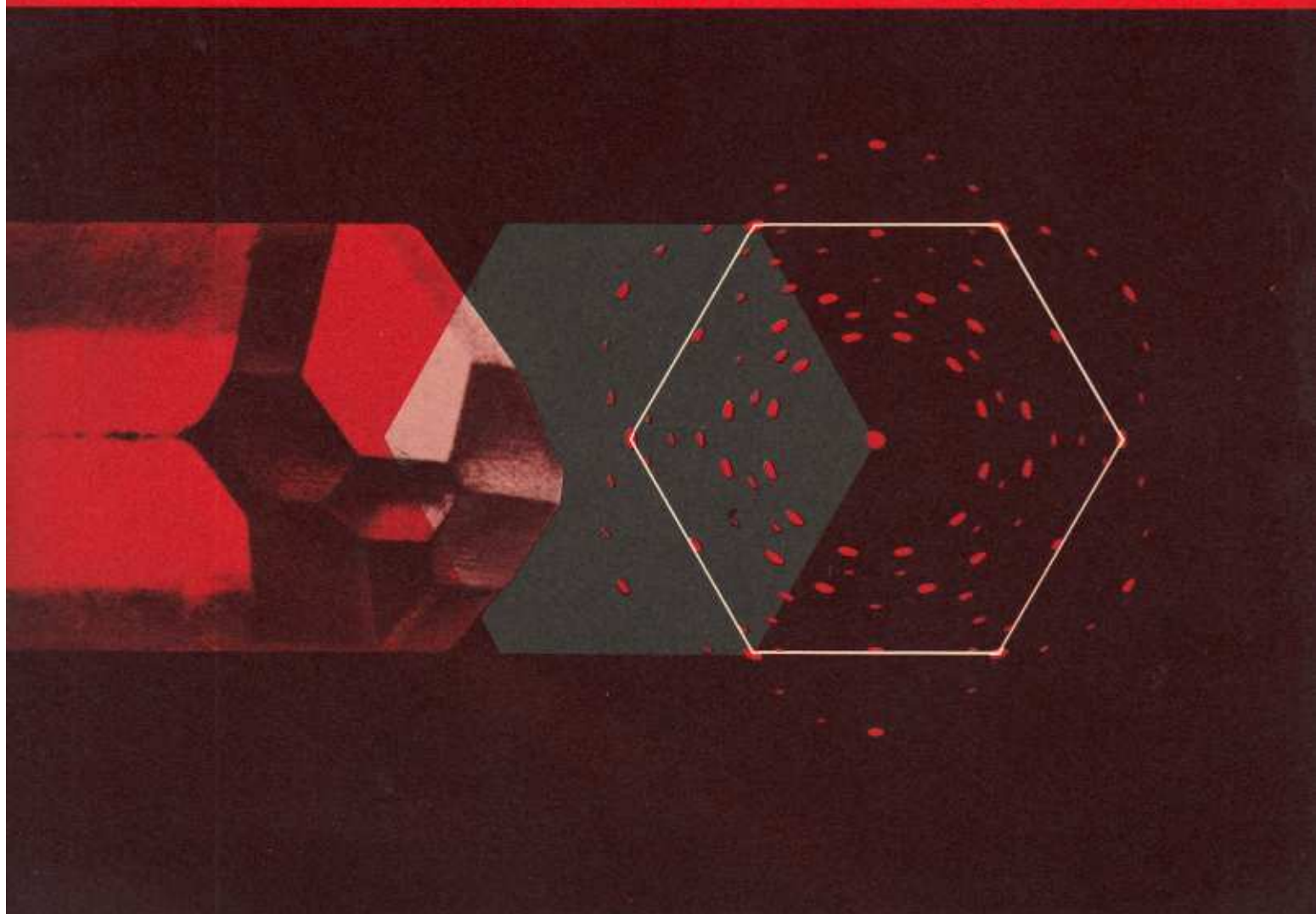




# The Start of X-ray Analysis



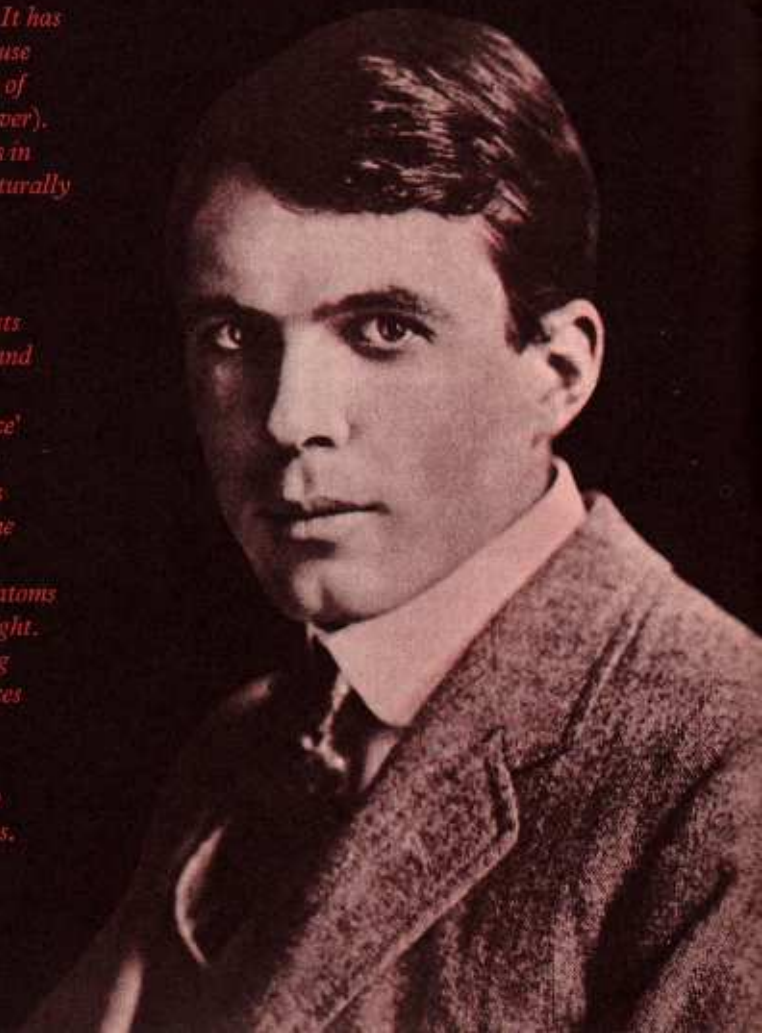
Sir Lawrence Bragg, the author,  
at the time of his Nobel Award.

**Introduction** – *How are the atomic particles in a crystal arranged? It has for long been guessed that they are arranged in regular patterns, because the outward shapes of crystals are so regular, like the hexagonal shape of the common quartz crystals or the crystals of the mineral beryl (see cover). Crystals of common salt have the shape of cubes, and alum crystallizes in very perfect octahedra with eight faces. This outward regularity is naturally explained by supposing that the atoms are arranged in regular patterns, like the decorations on a wall paper but in three dimensions.*

*It is only in the last fifty years that a way has been found to determine the positions of the atoms in the crystal. To do this, scientists use X-rays, which are waves of the same nature as light but ten thousand times shorter in wavelength.*

*When a beam of X-rays is passed through a crystal, the 'interference' patterns produced by the atoms can be used to find out the precise way the atoms are arranged. The interference pattern is made by the waves scattered by the atoms in the crystal, which reinforce each other in some directions and oppose in others. This interference can only take place when the wavelength of the rays is less than the distances between the atoms in the crystal, and this is why X-rays must be used and not ordinary light. The atomic patterns of countless substances have been worked out using this method, and from such knowledge many of the most recent advances in science have come about: for example, some glimmering of the way in which living cells work.*

*Sir Lawrence Bragg, the author of this book, was the first person to realize that X-rays could be used to find out the structure of substances. His father, Sir William Bragg, invented the instrument (called an X-ray spectrometer) with which investigations of crystal structure are carried out. Together they determined the structure of many substances and started the new science of 'X-ray Crystallography'.*





## The Start of X-ray Analysis

My interest in science started when I was at school, and I think the main reason was that my chemistry master taught in an interesting way. I went to school in Australia; I was born in Adelaide and my family lived there till we all came to England when I was eighteen years old. I did not have an easy time at school. I was good at lessons and so was put in classes where I was very much the youngest boy. I got into the sixth form when I was thirteen, and at fifteen my father decided it was not much good my going on at school, so he took me away and sent me to Adelaide University. I was entered there for a mathematics course, and got my honours degree in mathematics in 1908 when I was eighteen. I have mentioned these early times because, although physics has been my profession, I never did any physics at all at school and only a little at the university, where it was a kind of extra to the mathematics course. As another extra, I took English language and literature, which I think was a good plan.

Our chemistry master at school was very formal and precise. I remember at our first practical class he said: 'Boys, take up your mortars – now take up your pestles and see how much noise you can make banging your mortars.' We did so. He then said: 'Now you have found out how much noise you can make, let me never hear that noise again.' During the lunch break, he used to let me into the laboratory, and I set out all the experiments for the afternoon while he had a little nap lying on a form with two fat books under his head. He fascinated me when talking about the properties of atoms, and he did not mind my asking questions.

In 1908 we all came home to England because my father was invited to be Professor of Physics at Leeds University. In England I went to the university all over again, to Trinity College, Cambridge. I started with mathematics, but after a

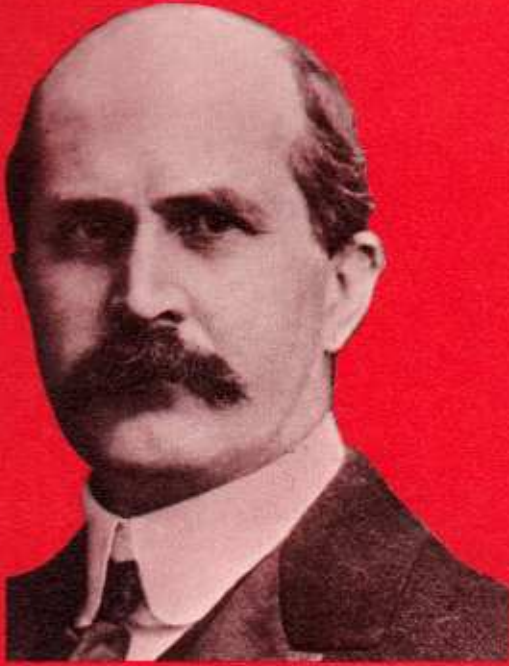
year my father thought it would be better if I switched over to physics. That was how I became a physicist.

When we were in Adelaide, my father used to talk to me about his scientific ideas. He had gone to Adelaide as a young man to be Professor of Mathematics and Physics at the university but, although he was a fine mathematician who had been third Wrangler at Cambridge, he had never done any physics at all. He always told us that he bought some books on physics and read them on the voyage to Australia, which was quite a long one in those days. He was so busy there building up the courses and practical work in the physics laboratory, and helping to develop Adelaide University, which was very new, that he never thought of doing research for nearly twenty years. But when he was in his forties he was asked to give an address to the Australian Association for the Advancement of Science on the exciting new discoveries which were being made in radioactivity. Preparing his lecture he began to wonder whether the explanations of the way the rays from radium behaved were right, and he determined to check some of the properties for himself. So he got the University to buy him some radium, and started experiments on the  $\alpha$  rays from radium. They were brilliantly successful. Rutherford was tremendously interested because they fitted in so well with his theory that radioactive decay resulted from the breakdown of the atoms of radioactive elements. At this time Rutherford was trying to convince a doubting scientific world that, in radioactive processes, one element was changing into another, an idea quite in opposition to the existing doctrine that atoms were unchangeable.

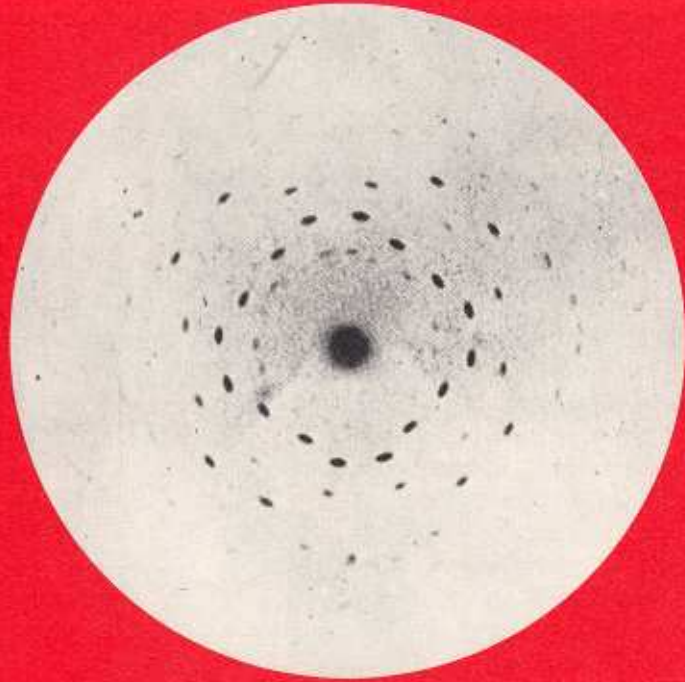
In two or three years my father became world famous as a pioneer in radioactivity. He was made a Fellow of the Royal Society and was invited to become a professor in England.



Figure 1  
One of von Laue's original photographs. Von Laue obtained the photograph by passing a narrow beam of X-rays through a crystal (here the crystal is zinc blende) on to a photographic plate placed on the far side. Dots on the photograph – as Sir Lawrence Bragg was the first to realize – are the reflections of the X-rays in the sheets of atoms in the crystal.



Sir William Bragg, the author's father, at the time of his Nobel Award.





I have wondered sometimes how different things might have been if my father had not been invited to give that lecture to the Australian Association for the Advancement of Science. It is just possible that he might never have started research, or done so even later in life. Anyhow, I have always regarded it as a very useful maxim that, if one does not know much about a certain subject but feels one ought to, the great thing to do is to promise to lecture about it.

My father went on to study the other radiations coming from radioactive bodies. (As scientists subsequently learnt, the  $\alpha$  rays are the nuclei of helium atoms shot out from disintegrating nuclei of radioactive substances, the  $\beta$  rays are electrons similarly shot out, and the  $\gamma$  rays are electromagnetic waves like light and X-rays.) He was particularly interested in the  $\gamma$  rays which, like X-rays, made a gas a conductor of electricity by turning the atoms or molecules into charged ions. Now my father showed by a series of very ingenious experiments that this is not a general effect all through the gas, but that certain gas atoms seem to get from the X-rays a kind of 'direct hit' which sends an electron careering along at a vast speed, and it is these electrons which ionize the gas. One would never expect waves to act in this way, so my father came to the conclusion that  $\gamma$  rays and X-rays were not waves but more like a lot of little bullets which hit an atom here and there: they were able to penetrate so far through solid bodies because they were electrically neutral, being a matched pair of positive and negative particles. I remember the very first time he told his great idea to me, just as we were boarding the old horse tram which ran down the main street near our home.

He went on developing this 'neutral-pair' hypothesis when he came to England, and had scientific fights with those people who believed in waves. So there was great excitement when, in 1912, a German scientist called von Laue published a paper with some beautiful photographs which, he claimed, showed that X-rays were undoubtedly waves (figure 1). He obtained these photographs by sending a narrow beam of X-rays through a crystal, and placing the photographic plate on the far side. When the plate was developed, it showed a number of spots in a pattern of the same symmetry as the crystal, and von Laue explained that the effect was caused by 'diffraction' of waves by the regular lattice of the crystal. My father got von Laue's paper while we were on summer

holiday on the Yorkshire coast, and we studied it together. I had just taken my degree at Cambridge and was then twenty-two. I, of course, was a tremendously warm believer in my father's theories, and we tried to find a way of explaining von Laue's photographs by something other than waves. However, when I returned to Cambridge for the autumn term and pondered over the photographs, I became convinced that von Laue was right in concluding that they were produced by waves. At the same time, I had an inspiration which led me to believe that when von Laue explained the peculiarities of his diffraction picture as being due to a complex set of wavelengths coming from the X-ray tube he was on the wrong track, and that really the peculiarities were due to the way the atoms were arranged in the crystal. If this were so, then X-rays could be used to find out the arrangement of the atoms.

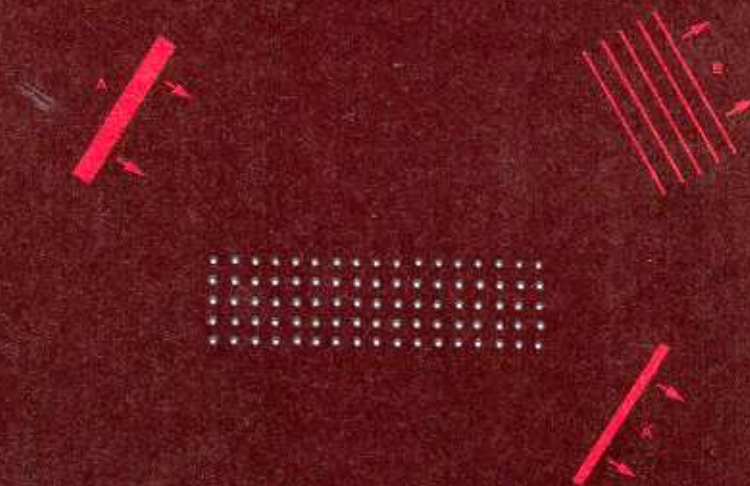
It is worth while describing this inspiration in some detail because it shows how scientific ideas often arise. They come because one hears about a piece of knowledge from one source, and happens to have a quite separate piece of knowledge from another source, and somehow the two just click together and there is the new idea. In my case, it was a kind of treble chance. First, J. J. Thomson had lectured to us about X-rays, and explained them as a wave-pulse in the ether caused by the electrons hitting the target in the X-ray tube and being stopped suddenly. Second, C. T. R. Wilson had given us very stimulating lectures on optics, including an analysis of white light which showed that one could think of it either as a series of quite irregular pulses or as a continuous range of wavelengths. Third, we had a little scientific society in Trinity, and at one of our meetings a member had read a paper about a theory that, in crystal structures, the atoms were packed together like spheres whose volumes were proportional to the combining power of the atoms. This theory had been proposed by Pope and Barlow and proved in the end to be quite wrong, but it suggested some very useful ideas. In science, a wrong theory can be very valuable, and much better than no theory at all. Hearing this paper, I realized that the atoms in crystals were arranged in parallel sheets. Anyone thinking about a crystal pattern would see this at once, but I had never thought about it before. So these three bits of knowledge were part of my background. When I was walking one day along the Backs at Cambridge -



Figure 2a  
Reflection of an X-ray pulse by a single sheet of atoms. Most of the pulse **A** passes through the sheet as **A'**, but a fraction is reflected as the weak wave **B**.



Figure 2b  
Reflection of an X-ray pulse by a series of atomic sheets. Each sheet reflects the pulse, giving rise to a series of waves **B**. These reflected waves are one behind the other, with the wave reflected from the top sheet in the lead.





I can remember the place behind St John's College – suddenly the three bits came together with a click in my mind. I suddenly realized that von Laue's spots were the reflections of the X-rays in the sheets of atoms in the crystal. Of course, the reflection of a pulse from a series of planes one behind the other turned it into waves of definite length, like white light being reflected from an opal or mother-of-pearl. The law which determines the relation between the wavelength  $\lambda$ , the spacing of the planes  $d$ , and the glancing angle  $\theta$  is  $n \lambda = 2d \sin \theta$ , where  $n$  is a whole number. It is a very simple optical law, but to my great pride it has been called 'Bragg's Law' ever since. Of course, the X-rays must be a continuous band of wavelengths like white light.

I have drawn a figure to explain how the law works (figure 2). Some of my readers, I expect, will not yet have done enough geometry to be familiar with 'sin  $\theta$ ', but this does not matter because I hope the general idea will be clear from the diagram. In figure 2a, the thick red line A represents the advancing X-ray pulse. The row of dots represents a single sheet of atoms in the crystal. As the pulse sweeps over this sheet, most of the pulse travels on as A, but a fraction is reflected as the weak wave B. Actually the crystal has thousands of sheets of atoms; I have shown five of them in figure 2b. Each sheet reflects the pulse, so we have five pulses, one behind the other with the wave from the top plane in the lead. The crystal is turning the pulse into a series of regular waves, just as the layers in an opal or in mother-of-pearl turn white light into the lovely red and green colours we see. Or, to put it in another way, the X-ray pulse can be considered, like white light, to be a mixture of all wavelengths, and the crystal is sorting out just the wavelength you see in figure 2b. This is only the same thing said in another way.

I tried out the idea, and at first there was a serious snag. It did not explain von Laue's photographs properly. Then I had another brainwave. Von Laue had used a cubic crystal of zinc blende. At the meeting of our small society, the reader of the paper had explained that cubic crystals need not be built on points at the corners of cubes alone, as von Laue had assumed; they could equally well have points both at cube corners and at the centres of cube faces. (See the white spheres in the diagram of common salt on page 6.) Directly this idea was used, the von Laue photographs were

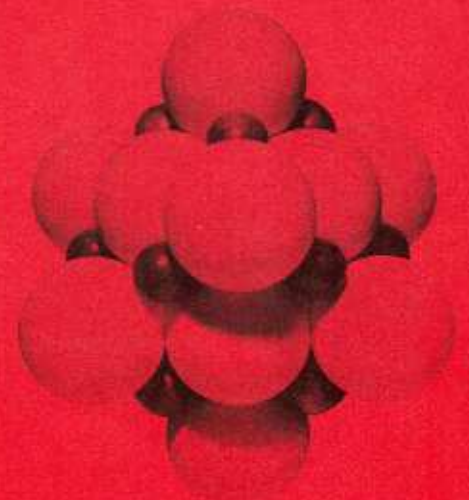
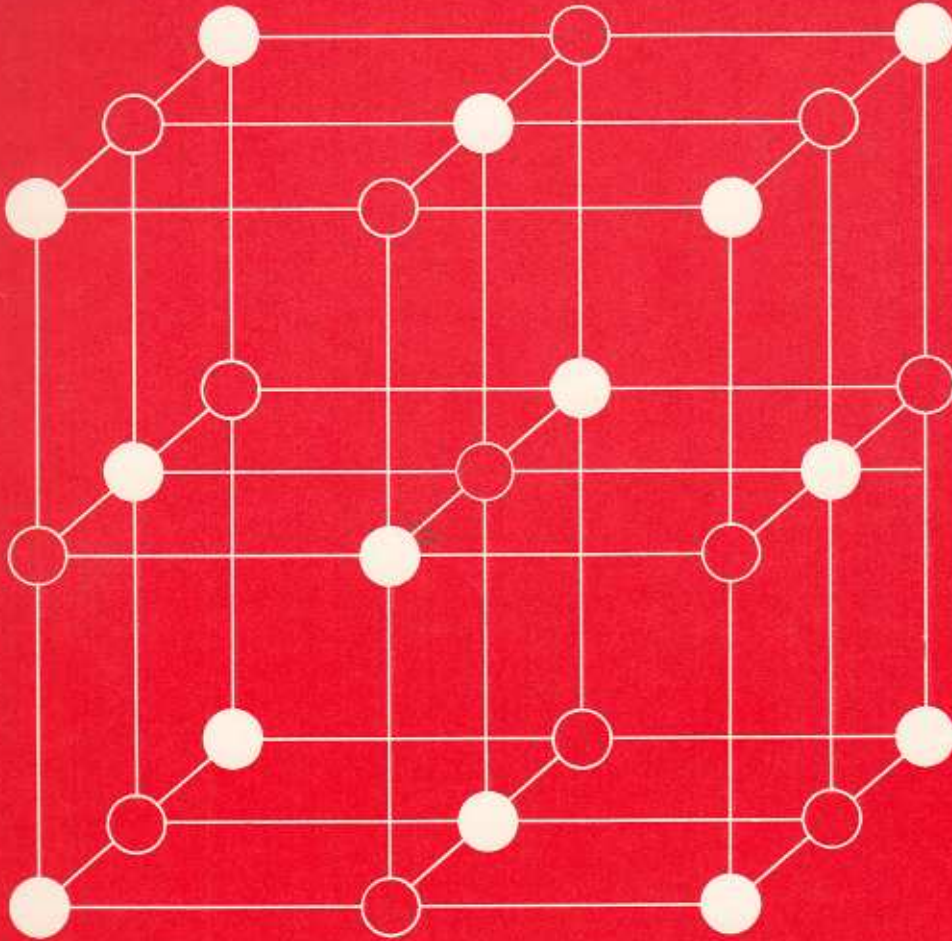
immediately explained. The scientific thrill of suddenly seeing the answers to a problem like this is tremendous: one goes about in a kind of dream. I realized that one could use the X-rays to find out the pattern of the crystal. I hastily wrote my ideas as a paper to the Cambridge Philosophical Society in November 1912, my first scientific paper. Professor Pope was deeply interested because of his theory of crystal structure, and he gave me specimens of potassium chloride and sodium chloride crystals. I got their Laue patterns, and deduced the way atoms were arranged in the crystals on a kind of three-dimensional chess-board pattern (figure 3). These were the first crystal structures ever to be analysed. Nowadays the structures of hundreds of substances are analysed every year, and X-ray crystallography has grown into a science which has had a great influence on physics, chemistry, mineralogy, metallurgy, and biochemistry.

At the suggestion of my teacher, C. T. R. Wilson, I tried the experiment of reflecting a beam of X-rays by a piece of mica in which one would expect well-defined sheets of atoms parallel to the surface. It worked! I can remember developing the photograph showing the reflection at a series of angles, and taking it still wet to display to J. J. Thomson. He glared at it, thrust his spectacles up on his forehead and scratched his head in a characteristic gesture, and grinned with pleasure. But what a task we had in those days to make our apparatus! No workshop was available to us, and we had to manage as best we could with a few tools we bought for ourselves and such oddments of wire, wood, and lead as we could scrounge in the laboratory. I got so excited with my first X-ray reflections that I worked the apparatus too hard and burnt out a platinum contact. The head assistant was very annoyed, and would not let me have another for nearly a month because it had cost ten shillings. Nowadays, a young scientist discovering an exciting new phenomenon like X-ray reflection would be given a grand apparatus and helped to go ahead as fast as possible. I had to make my lead slits and measure the angles with a card I bought for a shilling. The change has been very great indeed.

When I told my father about these results, he was of course very interested, and he at once started experiments to find out whether the rays which I had found to be reflected from crystal faces were in fact actual X-rays. When I wrote my paper, I did not want to take this for granted, so I



Figure 3  
The structure of sodium chloride – one of the first crystal structures to be determined by X-ray analysis. Note that the atoms of one kind (white dots) are at cube corners and face-centres.



Another way of looking at the structure of common salt – as a result of tipping up the cube on to one corner. Note the horizontal layers of similar ions.



called the paper 'The Diffraction of Short Electromagnetic Waves'. I avoided mentioning X-rays, having been very much teased at Cambridge for upsetting my own father's theory!

To make an accurate study of the waves, my father built what he called an 'X-ray spectrometer' (figure 4). It was designed like the spectrometer one uses to examine the wavelengths of light. A fine beam of X-rays fell on a crystal face which could be set at a measured angle  $\theta$ . The reflected ray was measured by what is called an ionization chamber, set at an angle of  $2\theta$ . The X-rays made the gas in this chamber a conductor, and the charge which flowed through it was measured by the electrometer at the base. It was a beautiful instrument. My father was very good at designing scientific apparatus, and he had at Leeds a genius of an instrument-maker named Jenkinson. His experiments on  $\gamma$  rays and X-rays had made him adept at accurate intensity measurements of these radiations. He soon satisfied himself that the reflected rays really were X-rays. He also made an exceedingly important new discovery. There was a very strong reflection of X-rays at certain definite angles, which could correspond only to X-rays of definite wavelength, like the lines in the optical spectrum of an element. These X-rays are characteristic of the metal in the 'target' of the X-ray tube from which the X-rays originate. This was the first determination of X-ray spectra. My father followed this up by determining the wavelengths of the X-ray spectra of a number of elements, and showing that they became regularly shorter as one passed from one element to a higher one in the periodic table of the elements. Moseley built on this discovery in his famous experiments which established the atomic numbers of the elements. (See the Background Book, *Inside the Atom*.)

However, although my father built the spectrometer in order to study the reflected waves, his instrument proved invaluable for use on crystal structure. For the earliest measurements with the spectrometer showed that it was a far more powerful way of finding out the pattern of the atomic particles in crystals than the roundabout and difficult method I had applied to the Laue photographs. I was at that time trying to interpret the Laue photographs produced by a diamond, and was quite bogged down. With my father's spectrometer, it was possible to measure the reflections of the

X-ray spectral lines from the diamond planes, and this led at once to a solution. The diamond structure aroused a great deal of interest and had a strong influence in convincing scientists of the value of 'X-ray analysis', as it came to be called.

I had a grand time in the holidays. My father's interests were still mainly in X-ray spectra, and he let me examine crystals with the X-ray spectrometer, and use measurements he had made to try to work out their structures. We worked furiously in 1913 and 1914, going back in the evenings to the

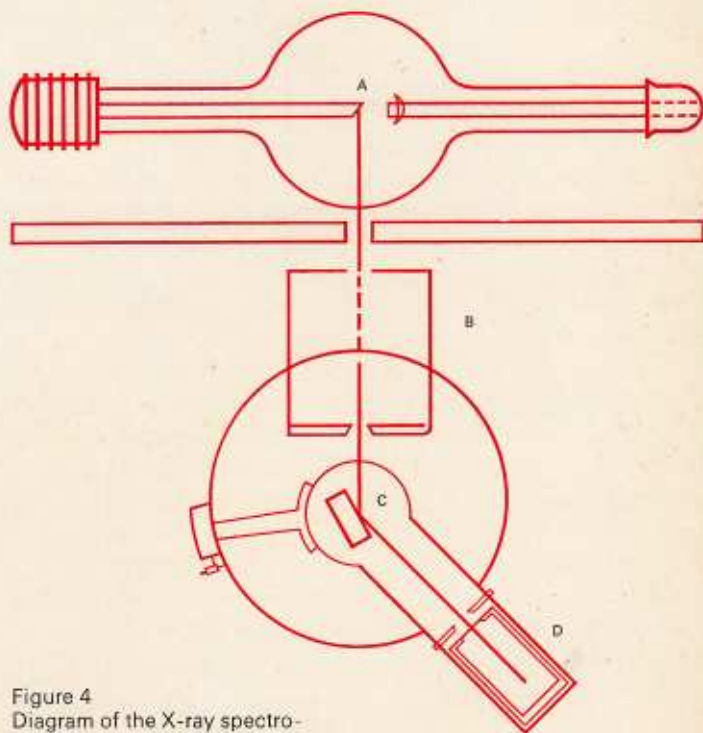


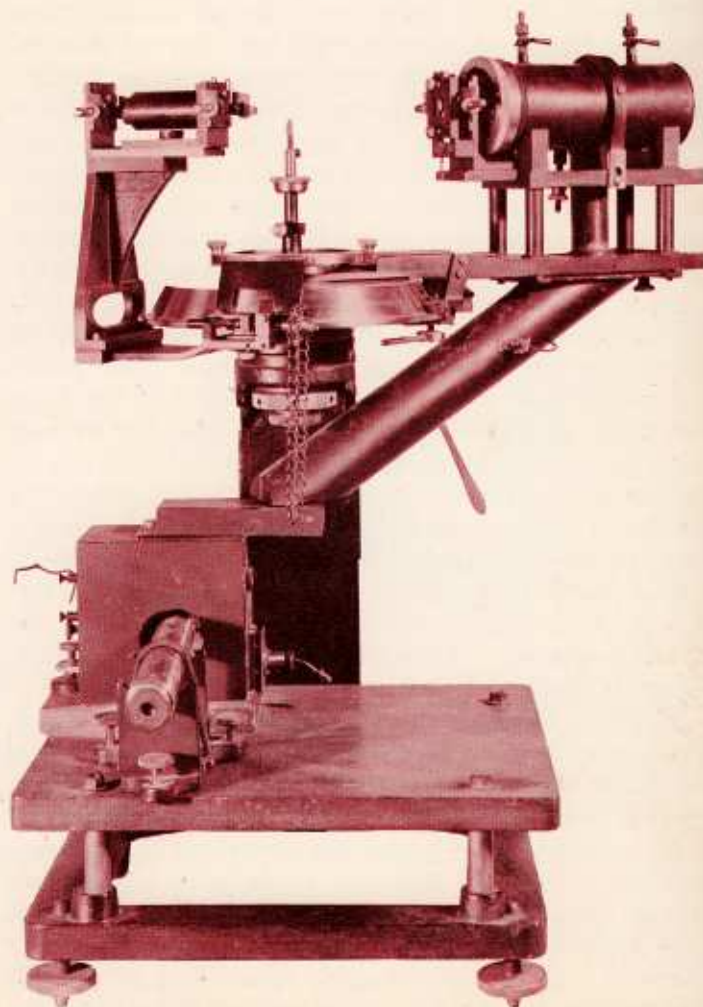
Figure 4  
Diagram of the X-ray spectrometer. X-rays generated in the tube **A** pass through the slit system **B** on to the inclined face of a crystal **C**, and the reflection of the X-rays is measured in an ionization chamber **D**.



deserted university to get more measurements. It was like discovering a goldfield with the nuggets just lying there to be picked up. One could not resist the temptation to pick up more and more, without a rest. I was very lucky. If it had not been my father who developed the X-ray spectrometer, I should never have been able to work with it. It is true that I should still have been the first to work out a crystal structure with X-rays, but this first success would have been quite swamped in all the advances the spectrometer made possible. In those years, 1913 and 1914, we worked out the structures of many kinds of crystal. We could make plans of the way in which the atoms were arranged in them, and this gave chemistry a 'new look'. For instance, chemists had talked of common salt, sodium chloride, as being composed of 'molecules' of NaCl. My very first crystal determination showed that there are no molecules of NaCl consisting of one atom of sodium joined to one of chlorine. The atoms are arranged like the black and white squares of a chessboard, though in three dimensions. Each atom of sodium has six atoms of chlorine around it at the same distance, and each atom of chlorine has correspondingly six atoms of sodium around it. Some chemists at that time were very upset indeed about this discovery and, as well as I remember, begged me to find that there was just a slight approaching of one atom of sodium to one of chlorine so that they could be regarded as a properly married pair.

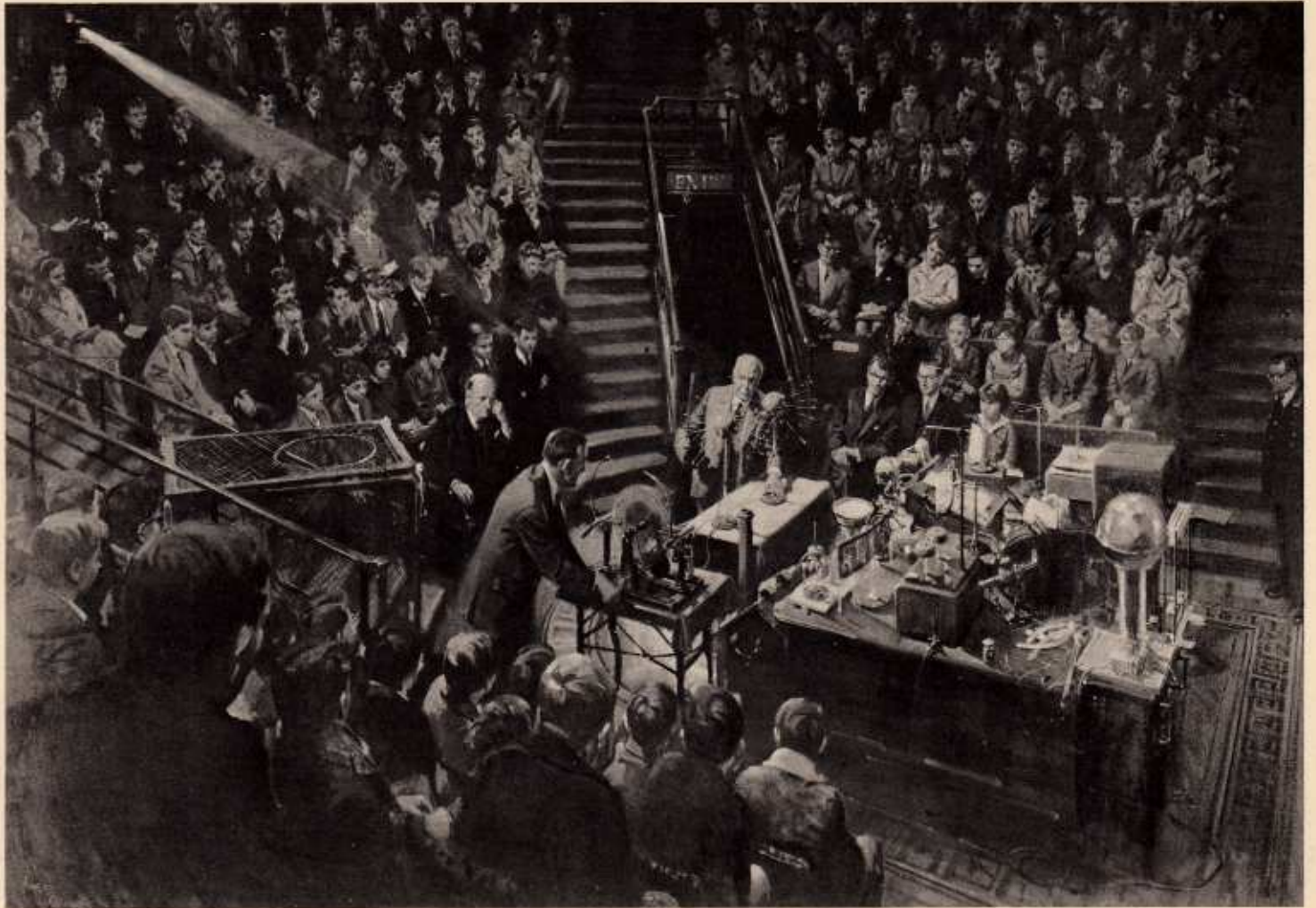
In August 1914 the war with Germany started and all research work stopped. I spent a year with a battery in England, and was then sent out to Belgium to start a way of finding the positions of enemy guns by sound - called 'sound ranging' - which I developed all through the war. In the winter of 1915-16, when I was billeted in the curé's house in a small village near Ypres, a letter reached me to tell me that my father and I had been jointly awarded the Nobel Prize for Physics. The curé, I remember well, went down to his cellar and came up bearing a bottle of wine with which we celebrated the occasion.

Early version of the X-ray spectrometer designed by Sir William Bragg. The diagram of the workings shows the instrument viewed from above. The lower part of the instrument is an electrometer for measuring the charge built up in the ionization chamber.  
*Royal Institution*





Sir Lawrence Bragg giving one of the 1961 Christmas Lectures at the Royal Institution where he is the Director.  
*From the painting by Terence Cuneo at the Royal Institution*





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