which an atom is surrounded by others. This precision has in many cases been a crucial factor in throwing new light on the nature of atomic groupings, and enabling us to see the pattern which runs through them. A striking instance of this was the formulation by Pauling of the laws which govern the structures of inorganic compounds, and the wonderful illustration of the operation of these laws in the structure of minerals such as the silicates. The bewildering features of alloy chemistry really had no good explanation until X-ray analysis supplied pictures of the structure which could be explained by the theoretical physicist. We are probably on the eve of a similar revolution based on the recent success of X-ray analysis in explaining the nature of bio-chemical substances. It is fascinating to see what important and far-reaching developments were initiated by v. Laue's discovery forty years ago.

[W.L.B.]

EXHIBITS IN THE LIBRARY
A display of apparatus, models and manuscripts connected with early work on crystallographic research, from the *Royal Institution Collections*.

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THE DISCOVERY OF X-RAY DIFFRACTION BY CRYSTALS

IT is now forty years since v. Laue made his discovery of the diffraction of X-rays by crystals. Members of the International Union of Crystallography celebrated the anniversary of this discovery last autumn all over the world, and in this country a special meeting was held at the Royal Institution, at which v. Laue was present. This seems a suitable occasion to review the early history of a discovery which has been of such importance to many branches of science.

I shall try to recapture the outlook at that time, the year 1912, recalling what was known about atoms and X-rays and the steps by which the original discoveries were made. Rutherford had published his nuclear theory in the previous year, showing that the mass and positive charge of the atom was concentrated at a very small body, the nucleus, at the centre of the atom. Together with J. J. Thomson's discovery of the electron, Rutherford's nuclear theory told us what the components of the atom are. The nuclear theory at once raised the problem, however, of the stability and definiteness of an atom composed of electrons circulating round a nuclear centre, and at that time Bohr was just arriving at that all-important and vital new concept of laws governing the behaviour of elementary particles which went beyond those of the Newtonian mechanics. It was in the subsequent year that he gave definiteness to the atom by quantizing the electronic orbits and showing how such concepts could explain quantitatively the spectrum of the hydrogen atom. If the atom was mysterious, the molecule was even more so. The forces which bind atoms together were wrapped in mystery, and indeed to many minds the molecular theory was still the hypothesis which explained the combining proportions of the elements. The

organic chemists had indeed gone further, and given a shape to the molecule with their structural formulae. These, however, were restricted to saying which atom was linked to which, a kind of topology which did not seek to define quantitatively the places which the atoms occupied in the molecule. The concepts of chemistry were indeed so formal in their nature that I can well remember the shock of delighted surprise when some years later Langmuir's papers appeared, in which he talked of molecules forming single layers on a water surface because one end of the molecule was soluble in water whereas the other was not. We had never dared to think of the molecule as having such a real nature, so to speak, and it was like a first glimpse of a new world.

The nature of X-rays was also very much a matter of controversy. They were suspected to be some form of electro-magnetic radiation, ether pulses set up by the sudden arrest of the electrons hitting the anti-cathode in an X-ray tube. Some aspects of their behaviour, however, were inconsistent with this view. My father, for instance, had proved in an indirect but very conclusive way that when the X-rays handed over their energy in ionizing a gas it was done by their handing over localized bundles of energy and starting β rays, and not by a general effect on the gas as a whole, such as one would expect if electro-magnetic waves were traversing the ionization chamber. This led him to conclude that X-rays and γ-rays were probably neutral doublets of oppositely charged particles, owing their high penetrating power to their neutrality and giving over their energy like the projectiles at particular points of collision. Eve, in his biography of Rutherford, quotes a letter of the 20th December 1911 written by Rutherford to my father: ". . . had a brief talk with Barkla. He seemed quite ready to believe that the energy of the X-ray was concentrated, but does not like your material doublet. He considers that an X-ray must be a type of wave motion, and has to be regarded as the simplest form of light. J.J. also expressed the latter view. . . ." These rival views were a symptom of the struggle in men's minds to reconcile the wave view and particle view, an antithesis which has been resolved by the quantum theory and wave mechanics. At that time, however, science had not made the decisive step of realizing that one cannot apply to small scale events and ultimate particles the laws of mechanics which govern large scale events.

As in most scientific discoveries, the element of chance seems to play a large part in v. Laue's great step forward. Just as only one of thousands or millions of the seeds produced by a plant carries on the next generation, so there are countless ideas floating around in the scientific world, and every now and then one of these falls on the fertile ground of a mind prepared to receive it, and starts some quite new development. At that time P. P. Ewald, now one of the senior figures of X-ray crystallography, was a Ph.D. student at Munich, where v. Laue was a junior member of the staff. Sommerfeld had suggested to Ewald as the subject of his dissertation the passage of light through crystals, analysing double reflection by considering the interaction of the waves scattered by the atoms arranged in a regular way in the crystal. Ewald had realized the inadequacy of existing theories of diffraction to explain what becomes of the incident wave in a crystal, and consulted v. Laue about his difficulties. This was the first time v. Laue had had his attention drawn to the existence of a "space lattice" in a crystal, a scheme of regular repeats of the elements of pattern in all three dimensions. Although he had attended lectures in Göttingen on mineralogy, the only branch of science which concerned itself with crystallography, the space lattice had never been mentioned in these lectures. Remembering back to those times, it is extraordinary how unfamiliar to scientists generally this conception of a regular crystalline arrangement was, simply because they had never had occasion to think about it. The geometry of patterns, which seems so familiar to us now, came with quite a shock of surprise. Ewald tells me that the lattice conception itself, which he had used as the basis of his theoretical study, was under grave suspicion because of the non-fulfilment of Cauchy's Relations.

Von Laue's reaction to Ewald's enquiry was to ask, "What are the distances between the lattice points? What happens if you take shorter and shorter wave-lengths? Why not try X-rays?" Interesting diffraction effects ought to be observed when the wavelength was small as compared with the crystalline pattern and not very much greater as in the case of light waves. It was suggested that Friedrich, a young scientist who had just graduated under Rontgen, should try the experiment of diffracting X-rays by a crystal. He had been engaged as assistant by Sommer-

feld, who promised that his services and the necessary apparatus would be made available. The physicists at Munich University at that time had the custom of meeting regularly after lunch at the Hofgarten Café where the white marble tables provided useful blackboards, a custom which still continued when I was at Munich for six months in 1930, and I believe it was at one of these reunions that v. Laue suggested that another student, Knipping, might try the experiment as Friedrich was involved in his research. This suggestion evoked the natural human reaction from Friedrich that he did not want to be left out, and so the two young men set up the apparatus together. They tried at first to direct the beam of X-rays at a crystal and observe diffracted beams thrown back at large angles on to a photographic plate. A crystal of copper sulphate was chosen, which they grew themselves, because it was thought that copper would have a strong fluorescent radiation. They had no success until Knipping, as a wild shot, tried putting the photographic plate on the side of the crystal opposite the X-ray tube, so as to catch beams diffracted at very small angles, when they at once got the famous first photograph of X-ray diffraction showing regularly arranged spots. When they powdered the copper sulphate these spots disappeared, so it was clearly an effect due to the crystalline arrangement. The experiment was repeated with a simpler cubic crystal, zincblende, and v. Laue showed that the positions of the spots were in formal agreement with those to be expected if diffraction took place at a regular cubic lattice. In the latter experiment Friedrich obtained Laue photographs of a technical excellence equal to that of any subsequent work, a tribute to his training under Röntgen. Ewald, who was by that time in Göttingen, heard through Sommerfeld about the results and developed the reciprocal lattice and sphere of reflection construction which is now so widely used.

I got involved in the story at this point. My father had shown me v. Laue's paper in the summer of 1912 when we were on holiday. I was a student at Cambridge at that time, but before going back I tried, at Leeds University in my father's laboratory, to see whether v. Laue's results could be explained by particles shooting down avenues in the crystal structure. My father was still attracted to his doublet theory, and reluctant to abandon the

idea that X-rays were material corpuscles. On returning to Cambridge I continued to ponder over v. Laue's photographs and became convinced that he was right in ascribing them to diffraction, but that his explanation of the selective pattern of the diffracted spots was erroneous. The cubic crystal of zincblende gave a pattern of spots, each of which was in the right position for diffraction by a cubic lattice, but in which only a small proportion of the total possible ones appeared, with an apparently arbitrary distribution of intensities. Von Laue ascribed this selection to the existence of some half-dozen specific wave-lengths from the X-ray tube. I showed that one could assume a much more probable continuous distribution of wave-lengths, and ascribe the peculiarities of the pattern to the structure of the crystal itself, which was more complex than a simple set of diffracting centres at the corners of cubes. My interest again arose largely through chance events. C. T. R. Wilson had given us a brilliant series of lectures on physical optics, in which he talked about the equivalence of pulses of light to a continuous white light spectrum, and this suggested that the diffracted spots could be considered as the reflection of pulses on the crystal planes. At the same time in our little scientific club one of our members had given a paper on Pope and Barlow's theories of valency volume, in which they explained the form of crystals by the assumption that an atom had a volume proportional to its valency. The theory was quite wrong, but their work was a mine of information about possible crystalline arrangements, and in particular suggested the face-centred cubic arrangement which proved the key to v. Laue's zincblende photograph. Professor Pope suggested to me that sodium chloride and potassium chloride might well be even simpler crystals than zincblende. I took their Laue photographs, and showed that their structures were like a three-dimensional chessboard of alternate sodium or potassium and chlorine atoms, the first analysis of a crystal.

Concurrently my father at Leeds was investigating the nature of these diffracted beams. Using the reflection idea, he built the first ionization spectrometer. A crystal at the centre of the instrument, which could be set at any desired angle, reflected the X-ray beam into an ionization chamber, where its strength was measured. Except for contributing the idea of reflection, which I had

proved by some simple experiments with mica, I had no part in the development of the ionization spectrometer, and my name only appeared on the original paper because I acted as his assistant in the vacation. The first great discovery made with the ionization spectrometer was that of X-ray spectra, specific X-ray wavelengths from the anti-cathode which corresponded to Barkla's K and L radiations from the elements. The same X-ray lines appeared on reflection from any face of a crystal; their position gave the spacing of the crystal planes parallel to the face, and their strength gave information about the crystalline arrangement. It was clear that the X-ray spectrometer provided a far more powerful way of investigating crystal structures than the Laue photograph. At that time my father was far more interested in the nature of X-rays than in crystal structure, and I was allowed to use some of the spectrometer measurements on NaCl for my paper on its structure. A crystal structure which aroused very great interest at the time was that of diamond, solved with the ionization spectrometer by my father. At about the same time I used the results of the spectrometer to get the structures of a more complex series, zincblende, iron pyrites and calcite. The explanations of the structures of these well-known crystals started the new science of X-ray crystallography, and showed how powerful its analysis could be.

The structure of diamond was widely acclaimed with satisfaction by the chemists, because it reflected in such a fascinating way the tetrahedral bonds of the carbon atom which the organic chemists had surmised. My structure of rocksalt had a very different reception. In this structure the atoms of alkali and halogen are arranged alternately at the corners of a set of cubes. Each sodium atom in rocksalt is surrounded regularly by six atoms of chlorine, and each atom of chlorine by six atoms of sodium. There is no indication that one sodium atom is paired with a definite chlorine atom; its attraction is shared by six equally spaced neighbours. To many chemists this conception seemed quite incompatible with the ideas of valency and the molecule which had proved so valuable to them. Professor Henry Armstrong in particular felt very strongly, and in a letter to *Nature* entitled "Poor common salt" he expressed himself in no measured terms about the rashness of young physicists who so

flouted accepted chemical concepts. Again, to try to recall how one felt at that time, it was quite exciting to think of alternate positive and negative ions in the structure of rocksalt, so that they were held together, not by directed bonds, but by general electrostatic attraction. How could they remain charged? Why did not the positive charge leak across to and cancel the negative charge? We were not particle-minded and it was hard to realize that charge could only move if attached to a particle, and that it was favourable in a balance of energy for the negative ion to take an electron from the positive ion and incorporate it in its structure, although this left both of them oppositely charged. The structure of rock-salt, in fact, foreshadowed the explanation by X-ray analysis of the nature of valency in inorganic compounds. It showed that the "molecule" is a reflection of something different in the inorganic compound, speaking generally, to that which exists in an organic compound, where, again in general, the molecule is a perfectly definite complex of closely-knit atoms which is only loosely attached to neighbouring molecules.

Darwin, about this time, had founded the theoretical quantitative basis of intensity of diffraction in two brilliant papers, but these were so far in advance of experimental measurement that they did not find their application until after the World War. Debye had calculated the effect of heat motion on X-ray diffraction, and my father had shown its existence experimentally. During the war my father first proposed the use of Fourier analysis, which has since become of such vital importance. Most work was, however, interrupted by the war from 1914–18, so this description of the early crystal analyses just before the war started seems to mark a definite point at which to end the story of the first start of the subject.

What has been the main contribution to science of the X-ray analysis of crystals? I think we may sum it up by saying that it is the precision which it has given to our pictures of the solid state. Many guesses had been made about the relative positions of the atoms in the solid state, and as has been mentioned above, the chemists had gone a long way towards elucidating which atom was linked to which in organic molecules. X-ray analysis has supplied a precise survey of the atomic positions, telling us the length of bonds and the angles between them and the way in