

CHAPTER 5

The Immediate Sequels to Laue's Discovery

5.1. W. H. Bragg and his Studies of Ionization by Gamma and X-rays

In 1912 William Henry Bragg was Cavendish Professor of Physics at the University of Leeds. Born in 1862 in Wigton (Cumberland) he was Laue's senior by seventeen years. His career was unusual in that he began research only after his fortieth year, although his great mental ability appeared from his early childhood on. After studying mathematics in Cambridge, and finishing there in 1884 with high honours, he was appointed, at the age of 22, as Professor of Mathematics and Physics at the young University of Adelaide, then in its tenth year. Here, Bragg's activity and interest was directed to physics, and to the perfection of his teaching and lecturing, in which he became one of the great artists. It was here also that he set up, soon after Röntgen's discovery became known, the first X-ray tube in Adelaide. Seventeen years passed after Bragg had become the head of the physics laboratory before the spark of original research reached him,—but from there on a mighty and steady flow of scientific results emanated from him until shortly before his death. The occasion which brought this change about was the need of reviewing, for a presidential address to the Australian Association for the Advancement of Science, the recent advances in radioactivity. He was struck with the possibility that a decision between the hypotheses of J. J. Thomson and of Ph. Lenard on the constitution of the atom might be obtainable from measurements of the absorption of α -rays in matter. In his paper of 1904 with R. Kleeman 'On the Ionization Curves of Radium' he showed that the exponential law which had been tacitly assumed for the decrease in intensity of an α -ray passing through matter was far from correct, and the characteristics of the range of α -particles were established.

The twelve papers Bragg published in the next four years led to the offer of the Cavendish Chair in Leeds which he accepted in 1908.

Here he extended the study of ionization in gases from α -rays to X-rays, using in the latter case the characteristic radiations, which, because of their homogeneous absorption, were considered to lead to more fundamental observations. He strongly favoured a corpuscular interpretation of X-rays for the reason explained in Chapter 2, and summarized his results on α - and X-rays in a book *Studies in Radio-activity* which appeared in 1912.

It is characteristic for W. H. Bragg's unbiased way of thinking, as well as for the impact of Laue's experiment, that it took Bragg only a very short transition period for accepting the pure wave theory of X-rays in explaining the diffraction experiments. Only in his first letter to *Nature*, dated 18 October 1912, does he make an implicit attempt to save the corpuscular idea by proposing an alternate explanation to Laue's for the zincblende diagram of fourfold symmetry, namely that 'all the directions of the secondary pencils in this position of the crystal are "avenues" between the crystal atoms' ('assumed to be arranged in a rectangular fashion') (cf. the discussion of this letter in the next section.). The same idea was expressed at the same time by another famous physicist whose previous work had also stressed the corpuscular aspect of radiation, Johannes Stark. His paper in *Physikalische Zeitschrift* 1912 (13, 973) assumes propagation of the radiation along 'Kristallschächte'—tunnels or pit shafts formed by the regularity of the atomic arrangement.

It is not quite certain how the news of Laue's discovery reached England, and, in particular, W. H. Bragg. Laue himself thought that it was through the off-prints of the Academy papers which he sent out very soon to all those whom he considered to be immediately interested. But these reprints may not have been immediately available. The daily press played no part. The *London Times*, in those years, carried a section 'Science, Arts, Music and Drama', but the first of these items hardly ever was considered a suitable topic for the *Times*' readers; the space of this column was filled with reviews of concerts, plays, exhibitions and auctions of art objects and silverware. No mention of Laue's discovery is to be found.

In July of 1912 the Royal Society celebrated in London its 250th anniversary. Among the representatives from Germany was Woldemar Voigt from Göttingen.* He must have known of Laue's work through Madelung, and through the talk Sommerfeld gave to the Physical

* P. v. Groth took part in the celebrations as representative of the Bavarian Academy, and it seems most unlikely that he should have abstained from publicising the important papers presented at the recent meetings of his academy.

Society of Göttingen not long after 8 June. It would only be natural that Voigt spoke of it to his British colleagues, especially J. J. Thomson. W. H. Bragg, who had been elected Fellow of the Royal Society in 1907, might also have been present at the celebrations. Full and detailed information on the work seems, however, to have come to Bragg through a lecture which J. J. Thomson gave to the physics group in Leeds (or Manchester) somewhat later. By that time reproductions of Laue's diagrams were available, and W. H. Bragg interested his son in them and together they undertook an independent discussion.

5.2. *W. L. Bragg and the Origin of Crystal Structure Analysis; X-ray Spectroscopy*

W. H. Bragg's son, William Lawrence Bragg, was following in his father's footsteps by taking physics as his main subject. Born in 1890 in Adelaide, he went to school there in 1900–05. He studied Mathematics (major) and Physics (minor) at the University of Adelaide and obtained his Bachelor's degree in Mathematics at the age of 18. On the return of the family to England, he entered Trinity College in Cambridge and received his final training in Physics at the Cavendish Laboratory under the 'grand old man' of physics, Sir J. J. Thomson, and the famous members of his staff, including C. T. R. Wilson, F. W. Aston and others. In 1911 he obtained his first appointment, to a lectureship in Trinity College.

But let us hear in W. L. Bragg's own words what the exciting sequence of events was after Laue's paper had reached W. H. Bragg in form of an offprint. He tells the story in an address given in 1942 in Cambridge at the First Conference on X-ray Analysis in Industry (held under the auspices of the Institute of Physics), which was published in 1943 in the series *Science in Britain*.

'At that time father held the view that X-rays had the properties of material particles rather than those of electromagnetic waves like light. He was led to this view by his experiments on the knocking of electrons out of atoms by X-rays (ionization), which he had shown to be a hit or miss affair affecting only a very small proportion of the atoms, not a general effect on all atoms as one would expect if X-rays were waves. I was a young student at Cambridge at the time, and of course an ardent supporter of my father's views. During the summer of 1912 we had discussions on the possibility of explaining Laue's patterns by some other assumption than that of diffraction of waves,

and I actually made some unsuccessful experiments to see if I could get evidence of 'X-ray corpuscles' shooting down the avenues between the rows of atoms in the crystal. 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. It is small clues that often lead to a solution, and perhaps I may be forgiven for repeating a figure (Fig. 5-1(1)) from my paper in the *Proceedings of the Cambridge Philosophical Society* (November 1912) which shows the clue I followed.

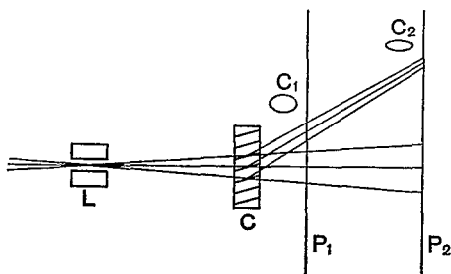


Fig. 5-1(1). Origin of the shape of the spots on a Laue-diagram.

'When the plate was placed at P_1 near the crystal the spots were almost circular like C_1 , but when placed farther back at P_2 they became very elliptical (C_2). 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 Fig. 5-1(1), 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. 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. Pope and Barlow had a theory that the atoms in simple 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 centre of the cube faces. I tried whether this would explain the anomaly—and it did! It was clear that the arrangement of atoms in zincblende was of the face-centered type. I was careful to call my paper on the structure of zincblende ‘The Diffraction of Short Electromagnetic Waves by a Crystal’, 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.

‘Pope, who was Professor of Chemistry at Cambridge, was very pleased at this support of his theories, and at his suggestion I tried crystals of NaCl, KCl, KBr and KI. The Laue pictures which they gave were simpler than those of zincblende, and led to a complete solution of their structure. These were the first crystals to be analysed by X-rays (*Royal Society Proceedings*, June 1913).

‘At about this time C. T. R. Wilson suggested to me that I might try the direct experiment of reflecting X-rays from a cleavage face, because such a face must be parallel to dense sheets of atoms in the crystal. I tried the experiment with mica, and I well remember J. J.’s excitement when I showed him the still wet photographic plate with a mirror reflection of X-rays on it (*Nature*, December 1912). My father thereupon examined a reflected beam, measuring its ionization and absorption, and proved conclusively that the diffracted waves had in fact all the properties of X-rays. As he put it, ‘The problem then becomes, it seems to me, not to decide between two theories of X-rays, but to find... one theory which possesses the capabilities of both’, a point of view with which quantum theory has now made us familiar, but which seemed very paradoxical at the time.

‘In order to examine the reflected X-ray beam more thoroughly, my father built the X-ray spectrometer. In this instrument, a crystal face can be set so as to reflect the X-rays at any angle (it is actually the sheets of atoms parallel to the face which reflect), and the strength of the reflected beam is measured by an ionization chamber. With this instrument he made the next great discovery. In addition to the ‘white’ X-radiation of all wave-lengths which I had called the 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 wave-lengths, just as elements give spectra in the optical region (*Royal Society Proceedings*, April 1913).

‘The X-ray spectrometer opened up a new world. It proved to be a far more powerful method of analysing crystal structure than the Laue

photographs which I had used. One could examine the various faces of a crystal in succession, and by noting 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 sheets parallel to these faces. The intersections of these sheets pinned down the positions of the atoms in space. On the other hand, a suitable crystal face could be used to determine the wave-lengths of the characteristic X-rays coming from different elements as sources. A 'pure' beam of monochromatic X-rays could be selected by reflection from a crystal and its absorption in various substances measured. It was like discovering an alluvial gold field with nuggets lying around waiting to be picked up. At this stage my father and I joined forces and we worked furiously all through the summer of 1913, using the X-ray spectrometer. Although the description of this instrument was published in our joint names, I had no share in its design. The capital I brought to the family firm was my conception of reflection and the application in general of the optical principles of diffraction, and my success in analysing the first crystals by the Laue method. It was a glorious time, when we worked far into every night with new worlds unfolding before us in the silent laboratory. My father was at first far more interested in X-rays than in crystals, and left the determination of crystal structure to me, with the exception of a paper on diamond which showed the power of the instrument he had devised. He measured the wave-lengths 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 wave-lengths ($K\alpha$ and $K\beta$) from various elements were similar, and that they were approximately inversely proportional to the square of the atomic weight. This was in fact a first hint of the subsequent brilliant generalization of this principle by Mosely, who used it to determine the atomic numbers. He measured *absorption edges*, the critical wave-lengths at which a sharp step in the absorption of X-rays by an element takes place. In fact, he laid the firm foundations of X-ray spectroscopy, afterwards to be so brilliantly developed by Mosely and Siegbahn. I remained true to my first love, the determination of crystal structure. By using measurements on crystals made with the X-ray spectrometer, many of them due to my father, I was able to solve the structures of fluor spar, cuprite, zincblende, iron pyrites, sodium nitrate and the calcite group of minerals. I had already solved

KCl and NaCl, and my father had analysed diamond. Between them, these crystals illustrated most of the fundamental principles of the X-ray analysis of atomic patterns. These results were produced in a year of concentrated work, for the war in 1914 put an end to research. I have gone into these early experiments in some detail because it is a story which I alone can tell, and which I wish to put on record.'

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Let us add some detail to this account by going over the letters to *Nature*. The first, in *Nature* of 24 October, is from W. H. Bragg and dated 18 October. In it an explanation of the zincblende photograph of fourfold symmetry is attempted according to the following rule: 'The atoms are assumed to be arranged in a rectangular (= simple cubic?) fashion; any direction which joins an atom to a neighbour at a distance na from it (where a is the distance from the atom to the nearest neighbour and n a whole number) is a direction which a deflected (or secondary) pencil will take, and it will, in doing so, form one of the spots. In other words, we have to seek for all the cases in which the sum of three squares is also a square, and we then recover the positions of all the spots on the diagram. For example, secondary spots take the directions (2,3,6), (4,1,8) and so on.'

It is then pointed out that (5,7,11) is present, although the sum of the squares, 195, is one short of a perfect square, and that (2,5,14) which should be there, is absent.

The letter concludes: 'The rule suggested itself to me as a consequence of an attempt to combine Dr. Laue's theory with a fact which my son pointed out to me, viz. that all the directions of the secondary pencils in this position of the crystal are 'avenues' between the crystal atoms.'

The construction proposed by W. H. Bragg is the analogue of the two-dimensional construction (Fig. 5-2(2)). Let a be the distance of nearest neighbours and na the radius of the circle drawn. If this circle passes through an atom P with integer components (n_1a, n_2a) , then $n^2a^2 =$

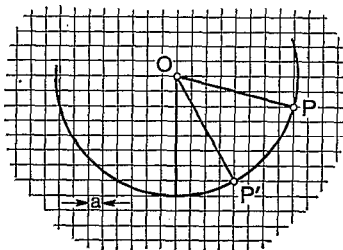


Fig. 5-2(2). Case of diffracted rays travelling along atomic avenues.

$= n_1^2 a^2 + n_2^2 a^2$, or $n^2 = n_1^2 + n_2^2$; adding the third dimension, the sphere of radius na passes through an atom P with components $(n_1, n_2, n_3)a$ whenever the equation $n^2 = n_1^2 + n_2^2 + n_3^2$ can be solved with integers. The direction OP thus determined is, according to the proposed rule, that of a possible secondary ray. It can be called an avenue between the atoms in as much as it is a rational direction in the lattice and the nearest parallel lines passing through atoms will be at a finite distance. (In the drawing it would be the parallel lines passing through atoms (4,1) or (4,7).) This minimum distance is characteristic for rational directions; irrational directions through one lattice point may never again meet a lattice point (otherwise they would be rational, even if expressed by large integers) and they lie densely side by side.

Now it is true that in the case of X-rays incident on a cubic crystal along the cube edge, the directions of all diffracted rays are rational—but the construction proposed does not prove it. It was purely empirical and covered only part of the diffraction effect. Evidently the hope was misleading of explaining the Laue diagram in terms of corpuscular rays shooting along atomic avenues without collisions.

The next paper to appear was W. L. Bragg's paper in the *Proceedings of the Cambridge Philosophical Society*, November 1912, from which he quoted in the address mentioned above. It contains three very important points: (i) the idea of explaining the Laue spots as *reflections* of the incident ray on the internal atomic net-planes; (ii) the assumption of a *continuous spectrum* of the incident ray and the *selective action* of the sets of reflecting planes in reinforcing only those wave-lengths which fit into their distances of repeat; and (iii) the proof that the lattice for zincblende is not the simple cubic one of Bravais, but his *face-centered cubic lattice*.

The concept of internal reflection does not contradict Laue's concept of diffraction, of which Bragg says he became convinced; rather it is only a different form of expressing the same results, and, as the successful application proved, a form simpler to visualize. It is in this paper that the Bragg formula $n\lambda = 2d \sin \theta$ occurs for the first time, though in the now less familiar form $n\lambda = 2d \cos \Theta$, where $\Theta = 90^\circ - \theta$ is the angle of incidence against the normal to the plane. It is stated that Θ has the same value for λ , $\lambda/2$, $\lambda/3$ etc.

Points (ii) and (iii) are closely connected. (ii) did away with the search for explaining the sharpness of the diffracted spots by assuming the generation of monochromatic radiation by crystal fluorescence. Instead, the crystal acts as a pass filter of great selectivity for the

incident radiation. This name was not in use in 1912, but the selective action of regularly spaced reflecting elements was well known in optics from such devices as Lummer-Gehrcke plates or echelon interferometers.—By trying the assumption of a face-centered instead of the simple cubic lattice, Bragg was able to account for the absences of spots which both his father and Laue had noted without being unduly worried. The face-centering atoms form their own system of planes which need not coincide with the parallel net planes supported by the corner atoms, and, if not coincident, they halve the distances of repeat. This may lead to destructive interference and the absence of a spot. Bragg gave the proof of the assumption of face-centering by showing that all the spots, and no more, were present which the crystal could pick out of a continuous spectrum, given certain angular and other restrictions.

Although this early paper does not yet contain a full structure determination, it comes very close to one, in the case of such a simple compound as ZnS .

W. L. Bragg presented his paper at the meeting of the Cambridge Philosophical Society on 11 November 1912. An abstract is given as a report on the meeting in *Nature* of 5 December.

In the discussion following the meeting C. T. R. Wilson suggested that if the internal planes reflected, external crystal planes might reflect as well, provided their roughness was small enough. This condition seemed likely to be fulfilled for crystals with good cleavage planes and W. L. Bragg reports successful experiments in a letter to *Nature* of 12 December 1912 (dated 8 December). He mounted a strip of mica of about 1 mm thickness on thin aluminium foil and exposed it to an X-ray beam at a grazing incidence of about 10° to the surface. After exposure of only a few minutes the trace of the reflected beam showed up on the photographic plate. That it was a specular reflection was shown not only by varying the angle of incidence, but also by bending the crystal to an arc and obtaining a fine focus.

In this experiment, the crystal was used as a reflexion grating—as had been tried without success in Friedrich and Knipping's first attempt. The reason why they failed was that they used practically normal incidence. Bragg notes that the reflection increases in strength as the glancing angle is diminished.

Bragg also investigated whether this was a surface or a body effect. A mica slip $1/10$ mm thick proved as good a reflector as a thicker one, yet, he writes, the effect is almost certainly not a surface effect, only the critical thickness has not yet been reached.

The idea of reflection of X-rays on the atomic net-planes of the crystal appealed to all English physicists by its simplicity, and the explanation given by W. L. Bragg of the occurrence or non-occurrence of diffracted spots on the Laue diagrams according to the selective action of the crystal was considered more reasonable than Laue's ad hoc assumption of characteristic wave-lengths of the crystal. Finally the introduction of the face-centered cubic lattice as underlying the structure of zincblende was the first step beyond the merely formal application of the lattice idea in Laue's theory, and therefore the first step in crystal structure analysis. The importance of this paper by W. L. Bragg for the further development of the field to which Laue had found the access can hardly be over-estimated.

W. L. Bragg's observation of specular reflection on the surface of the crystal opened up a period of closest collaboration between father and son which is perhaps unique in the history of Science, both for its lasting intensity and the importance of the resulting discoveries. It was a partnership of two outstanding scientists belonging to different generations, with an unrestricted give and take of ideas on both sides and a fundamental respect for the other's achievements.

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The first to be stimulated was the father, W. H. Bragg, who made certain that the reflected rays could be detected in an ionization chamber as well as photographically (letter to *Nature* 91, 23 January 1913). This experiment must have been the conclusive preparation for the construction of the X-ray spectrometer, the instrument which for decades to come was the main tool for crystal structure analysis throughout the British school and in many other laboratories. This was described in the joint paper 'The Reflection of X-rays by Crystals, I', *Proc. Roy. Soc. A* 1913, 88, 428-438. In this instrument the crystal is carefully adjusted on a goniometer head which can turn about a vertical axis; the horizontal X-ray beam falls through a slit system on to a vertical crystal face and is there reflected into an ionization chamber which can be swung round the same axis about which the crystal turns. Two types of measurement can be made: in the first the crystal face is set at a definite angle θ to the incident beam, and the angular position of the entrance slit of the ionization chamber is varied about the position 2θ ; if it is moved to angle $2\theta + \phi$, the ionization current is plotted as a function of ϕ , thus producing a 'reflectivity' curve. This curve is strongly influenced by the geometry

of the slit system, but in any case it reaches large values only if θ is one of the 'Bragg angles' which are determined by the relation now written

$$n\lambda = 2d \sin \theta$$

(n = integer called the order of reflection; λ wave-length; d the identity period of the set of reflecting net-planes of atoms and θ the 'glancing angle').

The other type of measurement is performed by opening wide the slit of the ionization chamber, so that at each position θ of the crystal the integral value of the reflectivity curve is measured by the ionization current, provided the chamber is always set at the angle 2θ . This gives a much quicker way of obtaining values for the overall strength of reflection. An important focussing property of the Bragg reflection was clearly recognized which was later much used in the construction of instruments; it has been fundamental ever since as a means for increasing the intensity and improving the resolution.

The spectrometer revealed for the first time the existence of very nearly monochromatic components in the X-ray emission from platinum targets, if the tube was run in a very 'soft' condition. By measuring the absorption coefficients of these monochromatic radiations Bragg found them to have values close to those known from other measurements for the L-series of platinum. While this gave the correct identification of these spectral peaks, the value of the wave-length, obtained by applying the Bragg Law, came out wrong because of a mis-interpretation of the meaning of a face-centered cubic lattice: in each of the four equivalent sites of the cubic cell of NaCl an atom of the average atomic weight $\frac{1}{2}(35.5 + 23)$ was placed instead of the whole molecular weight.

W. H. Bragg soon continued this investigation in a paper signed only by himself (*Proc. Roy. Soc. A* 1913, 89, 246), in which the correct structure of rocksalt is being used, that had meanwhile been determined by W. L. Bragg. Neglecting the splitting of the peak into two very close lines, Bragg now found the wave-length of the Pt L-radiation to be 1.10 Å, and those of nickel and tungsten to be 1.66 and 1.25 Å, respectively. These values received confirmation by the following tests: the energy $h\nu$ associated with wave-length 1.10 Å is $1.78 \cdot 10^{-8}$ erg, and this should be the minimum energy of the cathode-ray electrons capable of producing these X-rays. Now measurement of the absorption coefficient of the rays forming the peak gave 23.7 cm^{-1} in aluminium, and according to Barkla this absorption is found for the

characteristic K-radiation emitted by a target of atomic weight 74, or the L-radiation from an atom of weight 198. The atomic weight of platinum, 195, checks with the latter interpretation. Again, the energy required to produce radiation of this absorption quality is, according to results of Whiddington for the K-series, $2.14 \cdot 10^{-8}$ erg. This also stands in fair agreement with the minimum energy as obtained above from the wave-length.

It is interesting to note what a round-about procedure was necessary at that time for obtaining an independent checking of the first wave-length determination. With its success, the determination of the first crystal structure, that of NaCl by W. L. Bragg, also received an independent confirmation.

W. H. Bragg continued the exploration of X-ray spectra in several more papers, studying the L-spectra of the elements from which good targets could be made, like Os, Ir, Pd, Rh, Ni, and Cu; he investigated how the intensity distribution among the three peaks of the L-reflections depend on the composition of filters, or of the reflecting crystals themselves. In this paper (*Proc. Roy. Soc. A* 1914, 89, 430) he also discusses the relation between the scattering and absorbing powers of an atom. Whereas absorption changes abruptly at certain wave-lengths, scattering does not. Simple measurements show that scattering coefficients of different atoms are roughly proportional to the atomic weights. This is illustrated by comparing the 222 reflections in zinblende and diamond, and, in a most elegant way, by the vanishing of the 222 reflection in fluorite, CaF_2 , where the combined weight of the two fluorine atoms (2×19.0) just counteracts that of calcium (40.1).—These structures had meanwhile been determined by W. L. Bragg.

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Independently of the Braggs, two young physicists in Rutherford's Manchester laboratory had meanwhile begun work on the lines of W. L. Bragg's idea of reflection, H. G. J. Moseley and C. G. Darwin. Their main interest lay in the direction of making X-ray spectra useful for the infant atomic theory that was then being weaned in Manchester by Niels Bohr. The most suggestive, if not convincing, argument for the ideas which Bohr was applying to Rutherford's model of the atom was his success in interpreting the simplest and most fundamental of all optical spectra, that of Hydrogen. Moseley and Darwin sensed correctly that further support for Bohr's novel and

rather shocking application of principles derived from Planck's concept of energy quanta might be gained if the X-ray spectra were known. This soon proved to be true to an unforeseen extent, so that their work became one of the experimental pillars around which the quantum theory of the atom grew. An account of their work is given in C. G. Darwin's Personal Reminiscences in Part VII of this book.

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The great break-through to actual crystal structure determination and to the absolute measurement of X-ray wave-lengths occurred in W. L. Bragg's paper 'The Structure of some Crystals as indicated by their Diffraction of X-rays' in *Proc. Roy. Soc. A* 1913, 89, 248. The argument in the first part of the paper is based entirely on Laue diagrams taken by the author on KCl, NaCl, KBr, ZnS (blende), CaF_2 (fluorite), and CaCO_3 (calcite). First it is shown that any secondary ray, which in Laue's theory is described by three path differences $(h_1, h_2, h_3)\lambda$ between the wavelets from neighbouring scatterers, can also be regarded as split off from the primary beam by specular reflection on a set of atomic planes of Miller indices (h_1, h_2, h_3) . Next, a convenient graphical method is developed for the attribution of indices to the spots on symmetrical Laue diagrams by making use of the evident arrangement of such spots on nearly circular ellipses. The general theory of the Laue diagram is further discussed on the assumption that the primary ray is a 'pulse', that is, lacks any particular periodicity. This approach differs from Laue's in that the latter considered the diffraction of only one Fourier component of the pulse, so that actually the crystal is acted upon by a monochromatic incident wave rather than a pulse. At a time when the reasons for the occurrence of only certain definite wave-lengths in the diffracted rays were not yet fully clarified, it was essential to carry through the theory without the assumption of monochromasy of the incident X-ray.

The analysis of the KCl diagram of fourfold symmetry is taken first. It is shown to be a 'complete' diagram, that is, that all the spots are present which can be expected to occur by diffraction in a simple cubic lattice by variation of the two first indices in (h, k, l) within certain limits. This completeness proves that the scattering centres in KCl are arranged according to a simple cubic lattice.

The same completeness is not found for the diagrams obtained with KBr, KJ, CaF_2 , and ZnS. If, however, for ZnS only odd values of h and k are admitted, the 'index field' showing all combinations of

these odd values is completely filled within a certain region. This is correctly explained by assuming the scattering centres to be arranged according to a face-centered cubic lattice, and this result is corroborated by a discussion of the trigonal Laue diagram of zincblende in the Laue-Friedrich-Knipping paper. To that effect a rhombohedral axial system is introduced, consisting of the half face-diagonals of the cube, which include 60° angles with one another. It is remarked that a diagram of KCl, taken along the cube body diagonal can be referred to the same pattern of intersecting circles which yields the ZnS diagram, except for a change of scale of the filled-in region of the index field. This conclusion is found to be correct. If, on the other hand, a face-centered lattice is taken for the discussion of the KCl picture, and a simple cubic lattice for that of ZnS, no 'complete' regions in the index fields can be found; this disproves the suitability of this lattice choice.

The Laue patterns obtained with NaCl are neither of the KCl type nor of the type common to KBr, KJ, or ZnS. This is interpreted by assuming the scattering power of an atom to be proportional to its weight. Then K and Cl, of weights 39 and 35.5, are so similar that the crystal practically contains only one kind of scatterer; for NaCl (23 and 35.5) the difference can not be neglected, so that the crystal contains two kinds of scattering centres; whereas KBr and KJ again only have one kind of scatterer, because compared to the weight of the halogen (80 and 127, respectively) that of K (39) can be neglected.

This argument then leads to the correct structures of the four alkali halides. But Bragg declares that in spite of the apparent rigour of the argument the question remains unsettled whether the individual scattering centres are actually atoms or more complex units. The last third of the paper is devoted to the discussion of this point. It begins with a comparison of the trigonal Laue diagrams of fluorite, calcite and rock salt. The first two show great similarity between them and with the zincblende diagram, the last one differs. This leads to the conclusion that the scattering centres in ZnS, CaF_2 and CaCO_3 are arranged according to the same lattice, except that in calcite the angle between the axes is somewhat greater. Now it is characteristic of a lattice that every lattice point is surrounded by others in the same way. This could not be the case for the scatterers in the three crystals, except if scattering is concentrated in the only heavy atom which each of the crystals possesses. The conclusion is therefore that the active centres of scattering are the heavy atoms themselves. Scattering by NaCl is due to both atoms, and this makes its trigonal diagram different from those of the other crystals.

A check on this conclusion can be obtained by spectrometer measurements of the angles under which the various crystals reflect the same X-radiation. This gives the ratio d/λ , where d is the spacing of the reflecting net planes, and λ the unknown wave-length. Geometry then gives V/λ^3 , where V is the volume of the cell. Using the known density ρ and molecular weight M , the expression $V\rho/(\lambda^3M)$ is obtained which is proportional to the number of molecules in the cell. This is found to be very nearly the same for NaCl, ZnS, CaF₂, CaCO₃, and only half this value for KCl. Thus the conclusion is reached that KCl carries two equivalent centres of scattering, in contrast to the other molecules which contribute only one, the heavy atom.

Even so, Bragg continues, the proof of single atom scattering is not complete. It is not excluded that groups of four molecules each are associated with each lattice point or scattering centre. This would even be in keeping with the views expressed by Barlow and Pope on the dense packing of binary compounds, but it would be very difficult to visualize such arrangement in the cases of CaF₂ and CaCO₃. Thus, while no strict proof can be given of the correctness of the simple structures and of atomic scattering centres, the odds are for it.

A further argument can be obtained from the spectrometer measurements by comparing the total intensities reflected in various orders by the different crystals. It is seen that the strength of the reflection is influenced by the presence of the lighter atoms in a way depending on whether these fall on the same atomic net planes as the heavy atoms, or midway between them ('halving of distances'). This explains the differences of the spectrograms of KCl and NaCl; and in CaF₂, where the F-planes sandwich the Ca-planes at $\pm \frac{1}{4}$ the spacing, it suppresses some of the reflections.

Finally, W. L. Bragg derives from the knowledge of the NaCl structure the absolute value of the wave-length as $\lambda = 1.10 \cdot 10^{-8}$ cm; with the observed d/λ ratio this corresponds to a distance Na-Cl of $a = 2.783$ Å (instead of the better value 2.814 Å).

In the series of fundamental papers published by both Braggs in 1913 and 1914 this paper by W. L. Bragg unquestionably brings the greatest single advance. With its well documented, if not rigorously established answer to the challenge of the first structure determinations, it made all future structure determinations very much easier by providing an absolute wave-length scale. Henceforth it was possible to find the number of molecules per cell directly from the Bragg angles measured on the spectrometer. Together with the observed sub-

divisions of the repeat distances of certain sets of reflecting planes, an idea also introduced in this paper, the number of atoms or molecules per cell fixed the positions of the scattering centres in the simple crystals that were first investigated. It would, however, be an invidious undertaking to single out any one of the early papers as the most important one, so closely were they all interlinked and so rapid was the progress at the time of their writing which formed a background for their formulation.

* * *

W. L. Bragg's just analyzed paper was directly followed in *Proc. Roy. Soc.* A 1913 (89, 277) by a joint paper with his father 'The Structure of the Diamond'. According to a remark in Sir Lawrence Bragg's Personal Reminiscences in Part VII of this book, this paper was mainly his father's work. But it employed all the arguments developed in the preceding paper, and, if only for this reason, the joint authorship seems justified. The reflection by the octahedral planes of diamond shows the second order reflection to be absent, while first, third and fifth orders are observed. This absence is interpreted as meaning that between the simple series of 111-planes of a single lattice a second set of equally dense planes is interleaved with a shift of one quarter of the repeat distance. It is next shown from the values of the diffraction angles that the cubic cell contains eight carbon atoms, distributed over two interpenetrating face-centered lattices. The only way to comply with these demands is to let the two lattices have a displacement of one quarter the body diagonal of the cube between them. This gives each atom a position in which it is surrounded by four nearest neighbours lying at the corners of a regular tetrahedron. A Laue diagram of threefold symmetry confirms this structure by showing the absence of other reflections from planes with spacings similar to those of the 111-planes.

Diamond was the first example of a structure in which the effective scattering centres did not coincide with the points of a simple (Bravais type) lattice. The determination of this structure was acclaimed as a great triumph of the new methods. Whereas in the structures of rocksalt, zincblende and fluorite the absence of molecules in the accepted sense created an element of bewilderment, the beautiful confirmation of the tetravalency of carbon on purely optical principles made this structure and the method by which it was obtained immediately acceptable to physicists and chemists alike.

In further papers published before the work was interrupted by the outbreak of war, August 1914, the laws of absorption and the influence of absorption on the intensities of the reflections were investigated by W. H. Bragg, and the structures of CaF_2 (fluorite), FeS_2 (pyrites) and CaCO_3 (calcite) determined by W. L. Bragg. This latter paper with the title 'The Analysis of Crystals with the X-ray Spectrometer' (*Proc. Roy. Soc. A* 1914, 89, 468) shows remarkable progress in a number of ways.

(i) It is clearly recognized that for a complete structure analysis the intensities of the reflections have to be known and evaluated.

(ii) In view of the great difficulty of obtaining a meaningful theory of intensities, a practical 'normal' intensity ratio of 100 : 20 : 7 : 3 : 1 for the successive orders of reflection on a simple set of atomic planes is abstracted from experience. Deviations from these ratios show that the set of reflecting planes is a composite of several interleaving simple sets, possibly formed by different kinds of atoms.

(iii) The positions of the S atoms in FeS_2 , or of the O atoms in CaCO_3 , are not fixed at certain points of the cell by the number of molecules contained in the cell. They remain displaceable on certain lines of intersection of symmetry elements. In FeS_2 , for instance, the S atoms have to lie on the body diagonal of a cube formed by Fe atoms, and symmetrically to the cube centre; but their distance apart remains undetermined by symmetry and has to be found from a discussion of the intensities of reflection. The ratio of the S-S distance to the length of the cube diagonal is a 'parameter' of the structure. Pyrites and calcite were the first structures containing parameters, and only one each. For many years structure determinations remained restricted to cases where not more than two or three parameters occurred—tackling other structures was a hopeless endeavour.

(iv) Pyrites was for another reason a markstone in the development of crystal analysis. It was the first cubic crystal in which the axes of threefold symmetry in the four directions of the body diagonals of the cube, which are a characteristic feature of all cubic crystals, do not all intersect at the centre of each cubic cell; they are offset so as to pass one another skew without ever intersecting. The writer remembers receiving in Germany, long after the outbreak of war in 1914, a postcard from England from W. L. Bragg—the censor had seen to it that it could not contain any recent information—saying: 'I have nearly finished finding the correct structure of pyrites, but it is *terribly complicated*.'

5.3. C. G. Darwin's Work

While the series of discoveries contained in the early papers by W. H. and W. L. Bragg was by far the most important contribution to the field opened up by Laue's experiment, there were other physicists, of course, who took up the matter independently. The spectroscopic work of Moseley and Darwin has already been mentioned. Darwin alone published in 1914 two very fundamental papers 'X-ray Reflection' (*Philos. Mag.* 1914, 27, 315 and 675) which are entirely based on Bragg's reflection idea. Here, for the first time, is the successive reflection of an incident ray by a set of equidistant atomic planes treated with due consideration of the back- and forth reflections between the planes. This is, as will be discussed in Ch. 15, the beginning of a 'dynamical' theory of X-ray diffraction because the repeated scattering is taken into account, and not only the scattering of the incident beam, as in Laue's and Bragg's theories. These latter theories are correct only if a crystal is so minute that the building-up of large scattered amplitudes cannot occur. For a large crystal of undisturbed growth, called by Darwin a '*perfect crystal*', the reflection curve is found quite different from the one for a small crystal. Darwin calculated the reflection coefficient of a single atomic plane along the lines of a famous calculation by J. J. Thomson for the scattering of a single electron, and expressed the result for the crystal in terms of this coefficient. The measured reflectivity of the crystal could thus be compared to a theoretical value—and it was found to be too big by a factor of 10. It is much to the credit of the author that he was so convinced of the correctness of his calculated coefficient of reflection for the single plane, that he considered the factor of 10 to indicate that something was wrong in one of his fundamental assumptions, namely the model of the perfect crystal. He remarked that if the outwardly uniform crystal were supposed to be broken up into small domains which are not fully aligned with each other, then a *greater* reflected intensity is to be expected than for a perfect crystal. The reason for this is that even if the incident ray does not form the Bragg angle with a domain at the surface, it may still find a suitably oriented domain at greater depth which reflects it. Very small domains and de-orientations suffice for producing agreement between the theoretical and observed reflectivities. A crystal of such broken-up structure was later called a '*mosaic crystal*'. Darwin's formula for the reflected intensity became fundamental for crystal structure analysis, and a crystal obeying it was termed an '*ideal mosaic crystal*.' While the ordinary grown crystal

lies somewhere between the perfect and the ideal mosaic type, and its reflected intensity is therefore, within limits, unpredictable, it was shown later by W. L. Bragg that by a suitable surface treatment of grinding most crystals can be turned, superficially, into the ideal mosaic type, so that measured intensities may then be used in crystal structure determinations. Without such standardization of the measuring technique, crystal analysis would have been much delayed. —The formula for the reflection by perfect crystals became of importance only much later, see Chapter 15.

5.4. *Early Work in Other Countries*

Only a short synopsis of the development of X-ray diffraction work in some other countries will be given here; for more detail the reader is referred to Part VI.

In France, the earliest work on X-ray diffraction was done by Maurice de Broglie, who published no less than twelve notes in the *Comptes Rendus* of the French Academy between 31 March 1913 and 27 July 1914. He started out with the Laue-Friedrich-Knipping arrangement and showed, for instance, that the diffraction pattern of magnetite is not changed by applying a strong magnetic field to the crystal (which, incidentally, is mentioned as a proof that the diffracted rays are not formed of electrons). Other points in the first four papers are the use of two superimposed photographic plates in order to evaluate the absorption coefficient of the rays forming the spots, and the obtainment of diffraction by metals and organic compounds. De Broglie also tried in 1913, but with no success, to obtain diffraction of γ -rays; this was achieved some months later by Rutherford and Andrade in Manchester in a very ingenious and efficient way (see in Part VII Andrade's *Reminiscences*).

The series of de Broglie's brilliant papers on X-ray spectroscopy begins with a note of November 1913 describing a primitive photographic spectrometer—the first rotation diagram camera—with which spectra were registered, and with a second note of December 1913 containing the description of the Pt and W spectra obtained on an improved spectrometer with exposure times of the order of 15 minutes and a variety of analysing crystals. A great improvement in the technique of obtaining spectra is contained in a note of 25 May 1914 under the joint authorship of M. de Broglie and F. A. Lindemann (the later Lord Cherwell). This note introduces the method of secondary

excitation of the characteristic spectra by irradiating a sample placed outside the X-ray tube with sufficiently hard X-rays. In this way substances which are not suitable as targets can be investigated. It is shown that brass emits the characteristic lines of copper and zinc. The method is also convenient for obtaining absorption spectra because of the ease with which different wave-lengths can be obtained. The systematic study of X-ray spectra which Moseley had started is then extended to spectra which he was unable to obtain with the method of primary excitation. Finally, as an example of chemical analysis, a sample of some 40–50 mg of rare earth oxides, obtained from Urbain, is shown to be a mixture of gallium and germanium oxides. (For further details of de Broglie's work see Part VI, French Schools, and Part VII, Trillat.)

* * *

Another centre of early activity in X-ray diffraction development was Japan. (See also Part VI, Japan, and Part V, Nishikawa.) Here it was T. Terada in Tokyo who read a paper to the Tokyo Physico-mathematical Society at the meeting of 3 May 1913 in which he described the production of Laue diagrams of a large variety of crystals, among them alum, borax, sugar, turmaline, epidote etc. By using only a single large diaphragm with a hole of 5–10 mm diameter in front of the tube (at about 17 cm from the target), the intensity of the diffracted spots was such that they could be observed directly on the fluorescent screen. Visual observation made it easy to follow the changing pattern of ellipses of spots as the crystal was rotated. The idea that the spots were obtained from the primary beam by reflection on densely populated atomic net-planes was gained from these observations without knowledge of W. L. Bragg's papers which had not yet reached Japan at the date of the presentation of the paper. Why the densely populated planes should be preferred, 'regardless of the fact that the volume of different primitive parallelopipeda is invariant', is not obvious. Either it could be assumed 'that each of the crystal molecules placed at one point of the lattice consists, in its turn, of a group of chemical molecules arranged in the form of a similar lattice with a finite boundary', or else one could consider the radiation 'to consist of an assemblage of detached entities,—though it seems rather difficult to proceed in this way'.—These quotations illustrate well how many alternatives there were as long as one was still groping about for a satisfactory explanation of the fundamental processes.

Terada's junior colleague in Nagaoka's laboratory, S. Nishikawa, took up the study of X-ray diffraction effects in only partially ordered matter (paper with S. Ono on 'Transmission of X-rays through Fibrous, Lamellar and Granular Substances', read 20 Sept. 1913). Diagrams of asbestos and fibrous gypsum showing star-like streaks radiating out of the central spot are reproduced and explained on the assumption that the fibres contain elementary crystal arranged in all possible azimuths round the common axis of the fibre. Organic fibres, such as silk, wood, bamboo, or hemp gave very similar patterns, whereas flaky minerals like talcum and mica gave patterns of a different type which, by tilting the sample to the X-ray beam, could however be transformed into the first type. Very finely powdered samples ('granular substances') gave a ring or halo surrounding the primary spot similar to those already observed by Friedrich (*Phys. Zs.* 1913, 14, 317) with bees wax. Finally, in extension of observations by E. Hupka (*Phys. Zs.* 1913, 14, 623) of star-shaped figures obtained by letting the primary beam pass through platinum foil, a systematic search establishes the dependence of the diffraction pattern of polycrystalline metals on the mechanical treatment and the strains set up in the sample. 'Rolled zinc, for example, gives rise to six patches at a distance from the centre where a ring is observed in the case of zinc dust.'

Considering the fact that all this work had to be done with equipment borrowed from institutions all around, one can but admire the independent approach and the valuable ideas contained in these and other early Japanese papers. Terada's (English written) papers bear testimony of the author's thorough acquaintance with the German crystallographic literature; expressions like Zonenaxe, Punktreihe are added, in brackets, for clarifying the English terms. It seems likely that Terada knew Schoenflies' book on structure theory, and he recommended its study to Nishikawa* who later drew Wyckoff's

* Professor S. Miyake kindly writes to the author that he remembers Prof. Nishikawa as saying: 'It was suggested to me by Professor Terada to study Schoenflies' book. Prof. Terada seemed to anticipate that this theory would play a role in the structure problems of the future. So I went to the library of the Mathematics Department and found that the book had been bought for the library. There was no indication of its having been read by anyone before. I began studying it. At first, it was somewhat tedious to work through the theory, but I soon came to realize its implications for structure analysis. I wonder how Terada had acquired his knowledge of space group theory, or at least of its existence, at that time.

'When I went to England in 1919 and met Sir William Bragg, I handed to him a paper I had written, including a table of space groups, and asked him to publish it somewhere if he considered it to be meaningful. But it seems that my paper remained in his drawer. I suppose he did not well understand my idea at the time.'

attention to it. This was an important transmission of information much in advance of the time when the British crystallographers recognized the value of the systematic structure theory.

* * *

Of other sequels to the first Laue and Bragg papers the following should be mentioned here because they do not appear in the later Chapters on the development in the various countries after 1920.

The identity of all geometrical results in Laue's diffraction and Bragg's reflection theories was first formally demonstrated by G. Wulff (*Phys. Zs.* 1913, 14, 217), though both Laue and Bragg seem to have been fully aware of this result.—At the second Solvay Conference in Brussels, 1913, Sommerfeld gave a discussion of the original zincblende photograms with the twofold objective of showing that Laue's assumption of characteristic crystal radiation was unnecessary, and that the spectral distribution of the intensity in the Bremsstrahl radiation, i.e. the 'white' X-rays, could be reconstructed in a qualitative way from the estimated intensities of the diffraction spots. To that end the spots had to be split into groups according to the order of reflection, the absorption, and geometrical factors. Ewald worked this out more fully in a paper in *Ann. d. Physik* 1914, 44, 257. Looking back, the main result of this work was the full confirmation of W. L. Bragg's structure determination and of his physical picture of the pass-filter action of the crystal.

A very important contribution to the understanding of intensities was made by H. A. Lorentz when he lectured to his students in Leiden on the recent discovery and Laue's theory. He showed that the diffracted intensity of order h ($= h, k, l$) is proportional to h^{-2} , that is, that it diminishes with higher order. This 'Lorentz Factor' in the intensity helps to account for the limitation of observed spots to those of low orders. Lorentz' calculation, which was published in one of

Professor Miyake adds: 'As a guess, it might be that Prof. Terada had heard of space group theory from his mathematical colleagues in the Faculty of Science, unfortunately all dead now. Prof. T. Takagi, a famous algebraist, had been in Göttingen and belonged to Hilbert's school.' (See also Part V, *In Memoriam* for S. Nishikawa; Schoenflies was in Göttingen from 1884 to 1899.)

'By the way, Prof. Terada, who died in 1935, is very famous in Japan not only as a scientist, but even more so as a man of letters. He ranks among the top essayists since the Meiji era in this country, and his collected literary works, amounting to about tenthousand pages including letters and diaries, have had repeated editions, even up to the present, and so have many collections of his selected essays. He disseminated plenty of original ideas, scientific and non-scientific, fruitful and not fruitful.'

Debye's papers mentioned below, also made it clear why the intensity of a diffracted ray should be proportional to the scattering volume, i.e. to the total number of atoms in the crystal, N , rather than to its square as would be the case if the ray were formed by a superposition of wavelets scattered under the very best conditions of re-inforcement which are expressed by the Laue-Bragg conditions. In fact, integration over directions for which the re-inforcement is only partial has to be considered in order to obtain the observable intensity. This was well known in the theory of the optical grating, but its extension to the three-dimensional case showed H. A. Lorentz' great mastery of mathematical physics.

Meanwhile Debye, who had been called away from Sommerfeld's institute in 1911 to Zürich University (where he was succeeded in 1912 by Laue) had just settled as Professor of Theoretical Physics at the University of Utrecht in Holland. Here he tackled a problem which appeared to others hopelessly complicated at the time: the influence of the temperature motion of the atoms on the diffraction of X-rays. It will be remembered (but it was not known to Debye) that this influence had been expected by Laue's seniors in Munich to blot out any clear signs of diffraction. Debye was particularly well prepared to deal with this problem because he had already repeatedly combined statistical and classical methods in physics—then a relatively novel combination,—notably in his theory of the specific heat of solids. In four papers in 1913/14 he answered the problem of diffraction in a temperature-disturbed crystal. This resulted in the Debye 'Temperature Factor' for the diffracted intensity which has the form $\exp(-Mh^2)$, where h , as before, is the order of diffraction, and M a constant which can be expressed by means of the elastic properties of the crystal or their combination, the 'Debye Temperature', which occurs in the theory of the specific heat. As I. Waller in Uppsala showed in 1923, Debye's expression for M was wrong by a factor of two which became important for the quantitative relation of X-ray scattering and specific heat; but apart from this slip, Debye's achievement was a most impressive one and of great consequence not only in view of the future quantitative evaluation of diffracted intensities for crystal structure analysis, but also by paving the way for the first immediate experimental proof of the existence of zero-point energy, and therewith of the quantum statistical foundation of Planck's theory of black-body radiation. (Cf. Part VII, James.)

A brilliant star like Debye moved quickly from one university to the other in those days, in spite of the war. Thus, in 1917, we find

Debye occupying the chair of Experimental Physics in Göttingen. Here, with P. Scherrer, he developed the method of X-ray diffraction by powders. This was, simultaneously, but under the conditions of war quite independently, found in U.S.A. by A. W. Hull of the General Electric Co. It is interesting to compare the motivations leading to the successes in both cases, and the reader is referred to Part VII, the *Reminiscences of Hull and of Scherrer*. Neither Friedrich, when studying the wax halos, nor Hupka or Nishikawa when obtaining diffraction from polycrystalline metals, hit upon the powder method; the main reason for this is that none of them had tubes suitable for producing strong monochromatic X-rays, so that all they obtained were blurred halos.

It should not be forgotten that one of the greatest contributions from which all fields of X-ray diffraction profited, was that of William D. Coolidge of the General Electric Research Laboratories in Schenectady, N.Y. His new type of X-ray tube eliminated the necessity of juggling between a deficient and an excessive gas content by providing an independent electron source through emission from a white-hot filament. It thus made possible to run a tube in a stable régime with independent adjustments of power (milliampères) and voltage (kilovolts), which had been impossible with the old-time gas-containing tubes. It is obvious how important this was for the generation of characteristic radiation and for measurements requiring constant conditions over hours. It is less obvious, today, what a wealth of novel technological ideas and developments had to precede the construction of the first marketable tube. This was the time when high-vacuum began to emerge from the laboratories and enter into manufacturing processes, owing to the invention of powerful pumping systems (Gaede in Karlsruhe), getters (electric lamp industry), metals that could be outgassed (tungsten made malleable by Langmuir), and glass that could be sealed to metal (cf. Part VII, Hull)—in short it was the period when modern electronics was born.