Moseley's Determination of Atomic Numbers

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One of the earliest important consequences of Max von Laue's great discovery of X-ray diffraction was its use in verifying the theory of the atomic numbers of the elements. This was done by H. G. J. Moseley in Manchester towards the end of 1913, when he measured the frequencies of the K-spectra of the elements from calcium to zinc. It may be interesting to tell how this came about, and in describing it I propose not to adhere to the rule that no discovery can be claimed until it has been published. It seems to me that a juster picture will be given by a record of the conviction with which they had been held often months before any publication.

It must be hard for anyone now to realize the troubles facing physicists in those days on account of the conflict between the classical mechanics and the quantum theory. They seemed not to complement each other as we now recognize, but rather to present impossible contradictions. Thus in the case of the X-rays J. J. Thomson had assumed that they were straightforward electro-magnetic waves. He had calculated how they would be scattered by matter, and his predictions were very satisfactorily verified by Barkla. On the other hand the ionization produced by X-rays gave electrons of velocity so high that it was clearly contradictory to the wave theory as then accepted. Indeed for a time W. H. Bragg inclined to the view that the X-rays must be some kind of corpuscle. It was in this atmosphere of mutual contradictions that we were working in those days.

Up to the end of 1912 Rutherford's laboratory in Manchester had been almost entirely devoted to the study of radioactivity. The work covered many fields, but much the most important one undoubtedly was the discovery of the nucleus of the atom. Through counting the scintillations of scattered α -particles, work mainly carried out by Geiger and Marsden, Rutherford's brilliant calculation of their statistical distribution was verified, and it was also possible to determine roughly the nuclear charge, equal to about 100 electrons for gold and about 10 for aluminium. It was round this time that Niels Bohr first came to Manchester, and greatly influenced our thinking by his deep appreciation of the limitations of the classical theory. He did indeed then begin his theory of the hydrogen spectrum, but at first, though it looked most promising, we could not judge how far it would extend.

When we first heard of Laue's discovery, it appeared obviously of the very greatest importance, but there were still the conflicting views about the nature of the X-rays, and we had little idea of what would ensue, or that there would be any connection with the nature of the nucleus. Moselev had come to Manchester in 1910, and he had been working on radioactive subjects like the rest of the laboratory, but he now proposed to take up the study of X-ray diffraction as being the most exciting new field in physics, and I agreed to join him in this work: we did not in the least know what might come out of it. When we first approached Rutherford, he was distinctly discouraging on the ground that nobody in Manchester knew much about the technique of X-ray experiment, so that we would be severely handicapped as compared with other laboratories where they were familiar objects of study. However we decided to go ahead, and in particular to go beyond the photographic method by which the diffraction had been first discovered by Friedrich and Knipping. It seemed to us that ionization methods would give the advantage of being able to get quantitative measures, and that these would be necessary in order really to understand the subject.

Working with Moseley was a most impressive experience. He was without exception the hardest worker I have ever met. He had two principles in his work. The first was that when one starts to set up an experiment one must not stop for anything until it is set up. The second was that when one starts the experiment itself one must not stop till it is finished. There were of course no regular meals, and work often went on for most of the night. Indeed one of Moseley's expertises was the knowledge of where one could get a meal in Manchester at 3 o'clock in the morning. In spite of these strenuous rules, it was most agreeable to work with him, and there was a constant stimulus all the time in our discussions about the fundamentals of the subject.

Our interest was the general character of X-rays, and in particular we were inclined to accept the idea of white X-rays, which had been proposed by W. L. Bragg. We also adopted his method of studying the oblique reflection from the flat face of a large crystal. The two chief ones we worked with were of rocksalt and potassium ferrocyanide, both about 5 cm square. After various changes in the arrangements the work was done mostly with the crystal mounted on the axis of a turn-table. It was exposed to a narrow beam of X-rays coming from a platinum anticathode through a very narrow slit, and the detection was done in an ionization chamber set up on the turn-table at double the glancing angle of the crystal. With a view to getting strong effects with our narrow slits we used a narrow ionization chamber charged with helium which was raised to such a potential that it was on the verge of sparking. We had at first a good deal to learn about the technique of X-rays, but by a long variety of experiments we convinced ourselves that the rays we were studying were entirely similar to white light.

Through having adopted very fine slits we were unlucky in one respect, for by sheer chance at first we never happened to set our instrument in the position to reflect any of the characteristic rays of platinum. However it was not long before we were told about them by W. H. Bragg when he was visiting Manchester, and we could then easily verify his work and could identify the different orders of spectra of course much more readily than we had been able to disentangle the white X-rays. A small further point may be mentioned, in that W. L. Bragg had not yet worked out the crystalline structure of rocksalt, so that there was uncertainty about the absolute wave-lengths to a factor that might be even as much as $\frac{1}{2}$. However not long afterwards he solved this problem.

While we were engaged on this work Bohr had been developing his great theory of spectra, and as time went on there arose the possibility that the various X-ray spectra might be analogous to light-spectra but contributed by the internal electrons of the atom. Moseley therefore set out to determine these wave-lengths, but I had been spending some time calculating the optical effects to be expected and I decided to go on with that, since Moseley was now quite confident that he could do this work by himself.

As to my own work, we had made one set of experiments which gave specially interesting results; this was the determination of the ratio of the intensity of the reflected beam to the primary. The general calculations of the effects of arrays of atoms were not simple, including as they did the disentangling of the various orders of reflection of the white X-rays, but they hardly involved more than the mathematics of optical diffraction theory. It emerged that the pencil of reflected rays could not be more than 6" broad. Now even if one assumed that the reflection was perfect in this range, the total amount reflected was at the most generous estimate less than a tenth of what we had measured again and again. The calculation was made on the assumption that each atom scattered the rays independently of its neighbours, and it was therefore necessary to examine the effect of such cooperation, but this proved that the result would be to weaken the beam still further. Moreover in this second calculation the scattering proved to be proportional to f, the scattering coefficient of the single atom, whereas with the earlier calculation it had been proportional to f^2 , and there seemed to be evidence that this last was usually the correct answer. It was these results that led a good many years later to the study of imperfect crystals, with their primary and secondary extinctions.

Reverting to the work of Moseley, I followed it with great attention, visiting his room frequently, and noticing that nearly every time I did so the experiment looked completely different; this did not surprise me because I knew that he was always ready to take everything to pieces again if he thought of any possible improvement, no matter how trivial. At first he spent a lot of time using ionization methods in view of our previous experience with them. But in the end he turned to photography, and he found that for his purpose it was much easier. He had a large glass tube containing a railway with blocks of the elements from calcium to zinc mounted in a row along the carriage. At its ends there were stopcocks each carrying a reel at its inner end, so that he could move the carriage to and fro without losing his vacuum. Each element could thus be used as anti-cathode in turn by bringing ti opposite the cathode of the X-rays, and also opposite the slit which let the rays emerge. These rays then fell on his crystal so that they were reflected at the appropriate angles on to the photographic plate. The result was the photograph that has become famous in books on the subject. Before this time Bohr had explained the relation of the hydrogen spectrum to Rydberg's constant, and he had conjectured that the K-spectra might be essentially the same thing as the simple hydrogen spectrum though this could not be verified until their wavelengths were known. However, applying these ideas to his photographs Moseley was immediately able to say that the nuclear charges of his elements ranged by integers with quite high accuracy from 20 for calcium to 30 for zinc.

After this work at Manchester he moved back to his home in Oxford early in 1914 and, working in the Oxford University Physics Laboratory (Clarendon Laboratory), he continued the experiments there by studying the L-spectra of heavier elements. He thus completed this great task of establishing the principle of atomic number from hydrogen to uranium. He finished this work in time to join the party of the British Association that was to visit Australia in that year. But the war started and he returned home as fast as he could. He took a commission in the Royal Engineers, and was despatched to Gallipoli. There he was killed during one of the landings, a personal tragedy and a great tragedy for the progress of science.