Manchester Days

By W. L. Bragg

I feel very proud indeed that the issues of *Acta Crystallographica* next March are to form a 'Festschrift' in honour of my eightieth birthday, and greatly appreciate the kind thought which prompted this proposal.

Professor Wilson has suggested that it might be the occasion for some personal recollections, and I propose to reminisce about the Manchester days where many young people, afterwards to become well-known figures in X-ray crystallography, passed through the research school or were members of the staff. I went there as a very young and green Professor in 1919, and I left in 1937 to take the Directorship of the National Physical Laboratory. My first appointment to the staff was that of R. W. James, who was with me for the whole of my time at Manchester and was such a stalwart supporter. My last I cannot resist mentioning, though he was not a crystallographer. It was that of a young man from Bristol called Bernard Lovell who came as an assistant lecturer.

I shudder now to think not only how inexperienced in teaching I was when appointed to the Chair but also how four years of war had made us forget all our physics and indeed had made it hard to think about it seriously. It seems to me now that I made every mistake it was possible to make in planning the courses and the examinations. I sometimes was blamed, however, for what was not my fault. One of the landmarks in Manchester was the Girls High School, not far from the University, which was presided over by a famous headmistress, Miss Burstall, who was a most imposing and respected figure. Soon after my arrival day the Bursar sent for me and said 'What have you been doing? Look at this letter from Miss Burstall'. It ran something like this: 'The whole school is outraged by the way in which candidates for the Honours School of Physics are selected. Miss X and Miss Y applied for places from this school. Miss X was accepted and Miss Y refused, whereas all the school know that Miss Y had much superior claims. We can only conclude that the young and impressionable Professor is influenced by the physical appearance of the girls, because whereas Miss X is a fine upstanding girl Miss Y is somewhat puny'. I had duly to appear on the mat in audience with Miss Burstall, awfully arrayed in cap and gown, and explain that while Miss Y had done the scholarship exam and was clearly not up to Honours standard, we had no check on Miss X and so felt it only fair to give her a chance. I may say that Miss Burstall and I became warm friends afterwards.

It was very hard to start research. My first thoughts turned to an idea which was floating in the back of my mind just before the war. I had noticed that the distances between atoms in the alkali halides were additive to quite a close approximation, and this (Bragg, 1920) suggested that all atoms had definite sizes. One could assign a characteristic radius to each atom, such that the distance between two atomic centres in a crystal was the sum of the radii. In 1920 I published a list of radii, but unfortunately got my datum line wrong assigning too large a contribution to all the cations, and too small a one to the anions. I got my datum line from the distance between two sulphur atoms in iron pyrites, not realizing they were much closer than the sum of ionic radii. The distinction between ionic and homopolar bonds was not clear at that time, at any rate to me. Wasastjerna put this right by his analysis of additive ionic refractivities which showed that the anions were in general far larger than the cations. He visited Manchester to tell me his ideas, unfortunately on a day when I was in London, and though he subsequently wrote I was terribly slow in realizing the importance of his solution and so missed the chance of establishing an authoritative set of ionic radii at a very early date. They were of the greatest importance in the later analysis of more complex crystals, and as is well known Goldschmidt made extensive use of them in his brilliant analysis of the distribution of elements in the earth's crust.

My first research student was Professor Lucy Wilson from Wellesley College in Massachusetts. Looking back, I fear we were not ready to give her a really exciting research, and also I remember with remorse that we only had a very insufficiently heated room to offer her so that poor Miss Wilson had to work in a huge fur coat. I wish we had been able to offer her a better time.

The first serious research venture was a thorough quantitative analysis of X-ray diffraction in which James and I collaborated. We had been together in the war. I had been sent out to the front in 1915 to start a scheme called Sound Ranging, the location of enemy guns by sound, for the British Army. James joined our experimental section at Kemmel Hill near Ypres directly he got back to England from the rescue of Shackleton's antarctic crew, which was stranded on Elephant Island after their ship sank. He afterwards ran the training school when Sound Ranging proved to be a success and the teams were greatly expanded. Harold Robinson, my first assistant Director, and Nuttall who joined the staff soon after James, were also sound rangers, as were J. West and C. H. Bosanquet. It was one of the few scientific shows in World War I and attracted a number of keen physicists.

We had a sticky time in lectures because the students, many of whom were ex-service, were very rumbustious and played many tricks on us, but I had the perfect la-

boratory steward in W. Kay, who was up to all their games. Ernest Scott Dickson, another recruit to the staff, was also excellent at maintaining discipline. At the beginning of each year, a sheet was passed round the class which all were expected to sign, and I always remember his saying 'Miss Mary Pickford and Mr Charles Chaplin are honorary members of all classes and need not sign their names'.

James and I, with Bosanquet from Oxford who worked with us in the vacations, made an attack from 1921 onwards on the quantitative aspects of X-ray diffraction (Bragg, James & Bosanquet, 1921 a,b). We used the technique my father had developed of 'sweeping' the crystal through the reflexion angle so that all elements of the crystal mosaic made their contribution to the 'integrated reflexion'. I had an X-ray spectrometer made in my father's workshop in Leeds, and we added certain refinements such as using a string electrometer (a delightful instrument) and a potential divider to bring back the string to zero. The crystal was turned by a capstan, the spokes of which were moved in time with a metronome. It was a perpetual thrill to see the string barely moving, then much displaced as one went through the reflecting position, then almost coming to rest again; it made X-ray diffraction seem very real. The X-ray tube was activitated by an induction coil and my break, and keeping the gas in the tube at constant pressure was an art. It was a great boon when, later, Coolidge tubes became available. The results, however, were surprisingly accurate and we really sorted out primary and secondary extinction, using Darwin's formulae, and established standards for absolute intensity.

The result of these investigations was that, in examining a crystal, one could assign to any reflexion an absolute value of $F(hkl)$ in terms of the scattering by a single electron. Simultaneously, the f factors of atomic scattering at different angles were being established, first empirically, and later by calculation by Hartree. Armed with this precise information, one could tackle complex crystal structures with a number of parameters, instead of being restricted to simple crystals with one or two parameters. There was a great deal of scepticism about our claims, indeed I remember one German expert (I think in reference to my shot at phenacite, Be_2SiO_4; Bragg, 1927) saying that it was absurd to think of ever tackling crystals with more than two or three parameters! James's (1925) solution of barytes with eleven parameters was a first triumph of the new art. The extension of crystal analysis on a more ambitious scale was, I think, a major contribution of the 'Manchester School'. In 1928 West and I (Bragg & West, 1928) summed up our lore in a paper called *A Technique for the X-ray Examination of Crystal Structures with Many Parameters* (save the mark!).

We tackled silicates because I had such a kind friend in Hutchinson in the Mineralogical Department in Cambridge. He had strict orders from his Professor that nothing in the museum should ever be touched, but he supplied us under the counter with sections of minerals on which quantitative measurements could be made, cutting them perpendicular to zones. He was a warm friend and supporter all through my early research ventures, and I can never be sufficiently grateful to him.

The study of the silicates, another major contribution of the Manchester School, took place in two phases. The first was the realization of the dominant part played by oxygen in the structure of the earth's crust. Oxygen is both the most abundant and the largest atomic constitutent, and we regarded the structures as packed assemblages of oxygen ions with the far smaller cations in the interstices. I think that it was the analysis of olivine, Mg_2SiO_4 (Bragg & Brown, 1926a) which first confirmed this view; the oxygen atoms are in hexagonal closest packing. Chrysoberyl (Bragg & Brown, 1926b), monticellite (Brown & West, 1927), the chondrodite series (Taylor & West, 1928), and topaz (Alston & West, 1928) were all based on close-packed patterns. Another fascinating example was cyanite, Al_2SiO_5, which, although triclinic, has its oxygen atoms in cubic closest packing (Náray-Szabó, Taylor & Jackson, 1929). Beryl (Bragg & West, 1926) was a joy to analyse; when once West had determined its hexagonal symmetry elements, he and I spotted the structure in less than half an hour.

For the next eight years effort was concentrated on working out any silicates we could get hold of, till finally the master plan of silicate structure began to emerge. The turning point, which led to the silicon–oxygen scheme in all silicates, was the solution of diopside, $CaMg(SiO_3)_2$ (Bragg & Warren, 1928). Early in 1928 I went to M.I.T. in Cambridge, Massachusetts, as visiting professor. I well remember my welcome by Norton the head of the Physics Department. M.I.T. had a very industrial bent, and his main interest was refractory bricks, specimens of which crowded his office. He led me to a room with my name on the door, illustrated excellent arrangements for disposing of my coat and hat, opened drawers in the desk which were full of every kind of coloured pencil, stamped envelopes, writing and graph paper. A bell was pressed, an imposing secretary appeared, and he said 'She's yours'. He then, having done all he could for me, said 'I have forty young assistants and I want you to introduce them to original research'. I at any rate look back with complacency at having 'introduced' one of them who was a real winner, Bert Warren. I had brought with me a very complete set of measurements by West on the three main zones of diopside, but had failed to see the solution. Warren realized it, showing that the formula (SiO_3) arose from SiO_4 groups joined in a string, so that one had a continuous linear anion running right through the crystal. Warren came to Manchester the next year and extended his analysis to other pyroxenes and amphiboles (Warren, 1929, 1930a,b).

Such a galaxy of researchers tackled the silicates that I can only mention some of them. The chief was

W. H. Taylor, who started by solving the tricky aluminosilicates (Taylor, 1928, 1929). Taylor analysed analcite (Taylor, 1930) which cast a flood of light on structures of statistical symmetry. Taylor's great triumphs, of course, were his work on the zeolites (Taylor, Meek & Jackson, 1933), and then his success in solving sanidine (Taylor, 1933), the first feldspar, which completed the whole scheme of silicates. That dynamo of energy, Zachariasen, joined the group around 1930; we used to say we expected him to solve a new structure every fortnight. Machatschki had difficulties with an awkward structure, I think it was danburite (Dunbar & Machatschki, 1930). I remember that at his farewell party, there was a magnificent cake and he was asked to cut the first slice (with some guidance). When the section was withdrawn, it revealed a suggested structure for danburite in raisins, cherries, and angelica. Ito worked out hemimorphite, and West muscovite mica, though the structural scheme had been already spotted by Linus Pauling in his brilliant work on mica-like minerals. Pauling made a stay in Manchester in 1930. Others who worked on silicates in this period were Scott Dickson, J. T. Randall, Nahmias, Santos, Strunz, and Signer. Now that the scheme of the silicates is known, it must be difficult for crystallographers to realize our fascination at seeing the patterns unfold and the jigsaw fit together. I gave a popular address on *The Exploration of the Mineral World by X-rays* at the British Association meeting in Aberdeen in 1934, and had a really fine story to present. I have a vivid recollection of the occasion.

James followed up the quantitative aspect of diffraction, studying in particular the *f* curves of the atoms and the Debye temperature effect. The culminating point was the great paper by James, Waller & Hartree (1928) *An Investigation into the Existence of Zero-Point Energy in the Rock Salt Lattice by an X-ray Diffraction Method.* James's measurements, Waller's analysis, and Hartree's atomic models, were combined to provide the first direct proof that the atoms had a half-quantum of energy at the absolute zero.

Brentano came to us soon after I went to Manchester. He was very interested in gadgets and devised ingenious ways of photographic densitometry. He did not approve of the polluted Manchester atmosphere, and had worked out that it rapidly improved with height. So he installed a fan in an unused chimney in his house, and drew all the air down from a height of thirty-five feet, as being much purer.

Bradley came to the laboratory in 1923. He had a second in Honours Chemistry, an examination result which showed how fallible examination ratings could be. He started on the structure of elements, but after a stay in Sweden with Westgren he began his famous work on alloys. Bradley was a genius with the powder method, which he and A. H. Jay raised to a perfection of accuracy and analytical power which has probably never beeen equalled since. Jay's tragic death in a car accident robbed applied crystallography of a great

man. This group was undoubtedly the main centre in the world for studying that side of physical metallurgy which depended upon atomic arrangement. The work was in many fields. There was the analysis of structure represented by an early paper (Bradley & Thewlis, 1927) on α-manganese. This and other structures which he analysed, often with many parameters (Bradley & Gregory, 1931), provided the main evidence for Hume-Rothery's theory that alloy structure depended on electron–atom ratios and its explanation in terms of Brillouin zones. There was a vast body of work on the equilibrium diagrams of binary, ternary (for example Bradley & Lipson, 1938), and even quaternary alloys in which he showed the power of the powder method not only in distinguishing what phases were present but also in determining their composition by lattice spacing (*e.g.* Bradley & Jones, 1931). He studied structures in which the separation into phases was incomplete, leading to great internal strain, and explained in this way the coercive force of permanent magnets. Here he collaborated with D. A. Oliver, then director of research for Jessop-Saville of Sheffield. They very narrowly missed a tremendous scoop in the permanent magnet field. Bradley had shown that in the iron–nickel–aluminum alloys certain phases started aggregating in platelets perpendicular to the three cubic ones of the crystal, and at an informal conference held in Manchester the idea was mooted that if cooling took place in a magnetic field the platelets might show a preferred orientation perpendicular to one axis with a consequent greater remanence in this direction. Oliver tried it and found a beneficial effect of about 20 % (Oliver & Shedden, 1938), but this was not judged to be large enough to be commercially interesting. Philips in Holland then added more cobalt, which increased the magnetostriction, and arrived at an alloy in which the effect was several times as great in the preferred direction, so producing permanent magnets of formidable power. If I remember rightly, Philips in taking out their patents acknowledged that the effect had been published by Oliver, and so our industry was able to make a favourable deal for the rights of manufacture. A key paper was *An X-ray Investigation of the Cause of High Coercivity in Iron–Nickel–Aluminium Alloys* by Bradley & Taylor (1937). From 1931 onwards the group was extremely active, producing many papers on alloy structure. The accuracy of spacing measurement was greatly increased; an example was Jay's (1933) measurements of the thermal expansion of quartz. Bradley drew up an accurate procedure for allowing for absorption in the specimen. Another interesting structural determination by the powder method was that of phosphotungstic acid by Keggin (1934). The anion is a very large highly symmetrical complex.

The order–disorder story started in a curious way. C. Sykes was at that time a researcher in the laboratory of Metropolitan-Vickers in Trafford Park, and was investigating the use of iron–aluminum wires for heating elements in electric fires. He got some very strange

results with their resistance, which varied over a wide range depending on previous heat-treatment. He brought his specimens to Bradley, who found that when the alloy was cooled slowly, the iron and aluminum atoms segregated into ordered positions on a cube-centred structure of low resistance, whereas on rapid cooling they formed a disordered structure of high resistance (Bradley & Jay, 1932). At a colloquium when we discussed these results I suggested qualitatively the way in which order should decrease with increasing temperature, finally making a steep plunge and disappearing altogether beyond a critical temperature. E. J. Williams was present, and next morning he came to me with the complete quantitative theory which he had worked out overnight. We were very excited, but could not believe we had hit on something which had been overlooked, so I wrote to several British metallurgical colleagues to ask if these effects were already known. They all replied in the negative so Williams and I published our theory in three papers *The Effect of Thermal Agitation on Atomic Arrangements in Alloys* (Bragg & Williams, 1934, 1935; Williams, 1935).

I then had a reproachful letter from Borelius in Stockholm. He pointed out quite rightly that not only had he published a similar theory, but he had sent me a copy of his paper a year or so previously! I was not thinking about alloys at that time and had put it aside for later study. However, Williams's analysis went deeper, and I think our way of looking at it was more easily grasped, because we started a burst of work on other manifestations of the order–disorder phenomenon as a phase transition of the second kind. Sykes (Sykes & Jones, 1936) built a very fine apparatus for studying the specific heat of ordering alloys as a function of temperature. A crowning point was Bethe's (1935) analysis which introduced the idea of short-range order. At that time the laboratory had the unique distinction of housing both Bethe and Peierls, who also worked on order–disorder; we were indeed strong on the theoretical side. Mott came as a lecturer in 1930 and began his studies in metal physics, and of course we had D. Hartree and E. J. Williams, a real galaxy.

Williams was a great character. It was terrifying to be a passenger in his car. He had a way of passing a tram on the outside as another was approaching from the opposite direction, and just squeezing between the two when a crash seemed inevitable. I remember the day he came as a Ph.D. student in 1924. He presented himself with a large bandage on his head. He had arrived the night before, and hearing that a rag was on between the University and the College of Technology he had of course joined in with the utmost verve. He produced brilliant papers on the passage of radiation through matter, alone and in collaboration with Nuttall. He had a vivid imagination and a most fertile mind.

We had periodical visits from two young students in Liverpool, Beevers and Lipson. They were working on X-ray analysis in a vacuum; as there was no-one with similar interests in the Liverpool Laboratory, they came with their results and models to have a discussion with the Manchester experts. If I remember rightly, their interest was in alum structures at first (Lipson & Beevers, 1935). Later (Lipson & Beevers, 1936) they worked out a more systematic way of calculating two-dimensional Fourier diagrams which greatly shortened the labour, and in turn this led to the 'Beevers–Lipson Strips' which were so widely used before computers became available.

We started to use two-dimensional Fourier series in 1928 (we had already extensively used one-dimensional series). When working with Warren in Cambridge (Massachusetts), I had been puzzling over the possibility of two-dimensional maps, because the measurements on diopside provided complete sets of F values around the three principal axes. I got no further, however, than using the (h00) and (00l) amplitudes for a kind of tartan plaid; I completely missed the necessity of crossing them with ($h0l$)'s. It was my father who realized that this was the crucial point, and soon after my return he wrote asking me whether intensities or amplitudes ought to be used. I replied to say that amplitudes were correct, and that I had a complete set of measurements on which the idea could be tried out – could we not join forces? He was too generous, and let me go ahead to sum the Fourier series for the diopside projections (Bragg & West, 1930). Warren and I had solved the structure so the signs were all known. It was a thrill to see the positions of the calcium, magnesium, silicon, and oxygen atoms showing up as contoured mountains of appropriate size. I worked out all the values of $F \cos \theta$ with a slide rule; it took about a week. I have always felt remorseful, that I did not either give the material to my father to develop, or insist that the results appeared in a joint paper, because the key idea was entirely his.

I attach a list of the main people who did X-ray analysis or took part in related crystallographic investigations during my time at Manchester, hoping it will be of interest. The names are arranged according to the academic year in which they joined the staff or the research body, or in some cases (*e.g.* Pauling) paid a visit for a month or two. It is over thirty years since I left Manchester, and I am sure that my imperfect memory has led me to make mistakes and omissions, which I hope will be forgiven. It was a wonderful time, and a wonderful group with whom to work, and I look back to those years with a deep gratitude for having had the experience.

Researchers at Manchester, 1919–1937

1919–20 R. W. James.
1920–21 E. Scott Dickson.
1921–22 J. C. M. Brentano.
1922–23 A. J. Bradley.
1923–24 Lucy Wilson, Orrell Darbyshire, G. Greenwood.

1924–25	D. R. Hartree, E. J. Williams, G. B. Brown, Samuel Causey, Dorothy Heyworth, W. A. Wood.
1925–26	Anthony Claasen, Joseph West, Walter Binks, J. T. Randall, J. Thewlis.
1926–27	Ivan Waller, Elsie Firth, W. H. Taylor, J. M. Cork.
1927–28	Phyllis Jones, N. A. Alston, G. W. Brindley, J. M. G. Bruckshaw, J. A. Darbyshire, Rachel Boullen, T. Boyer, W. W. Jackson.
1928–29	I. Náray-Szabó, Felix Machatschki, W. H. Albrecht, F. W. H. Zachariasen, A. H. Jay.
1929–30	N. F. Mott, Linus Pauling, B. Warren, C. Dunbar.
1930–31	J. S. Hey, C. Gottfried, C. H. Gregory.
1931–32	T. Ito, J. R. de A. Santos, M. Nahmias, J. F. Keggin, A. L. Roussin, E. Eastwood, R. W. Gurney, C. V. Helvig, R. M. Parker, W. J. Whitehouse, C. A. Meek.
1932–33	Hans Gross, Rudolf Signer, Hugo Strunz, J. W. Illingworth.
1933–34	Rudolf Peierls, H. Bethe, W. Berg, Abraham Taylor, S. W. Rodgers.
1934–35	C. A. Beevers, I. Fankuchen, G. King, H. Horrocks, H. Grime, E. Pickup.
1935–36	H. Lipson, S. S. Lu, S. H. Yü, C. Sykes, M. S. Ross, C. S. Cheng, R. Hardy.
1936–37	H. J. Goldschmidt.

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