

The Manchester School of W. L. Bragg

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When I arrived at Manchester in November 1928 to study crystal structure work in the Physical Institute of Victoria University, W. L. Bragg was a young professor still in his thirties. His outstanding research work and the discoveries he made (when 23 years old) with his father in the field of crystal-structure determination by the application of X-rays were recognized in 1915 by the award of the Nobel Prize, and I hardly believe this age limit will be lowered in the foreseeable future.

Besides other physical research the main work in the Physical Institute was crystal structure determination. A fair number of prominent scientists worked here, such as R. W. James, J. West, G. W. Brindley, W. H. Taylor and others; also guests like F. Machatschki, W. H. Zachariasen, L. Pauling and so on. It was a great honour for me to be able to work in this distinguished company, under the brilliant leadership of W. L. Bragg.

Bragg was sincerely interested in every field his co-workers were engaged in; he discussed their problems with them every day, his hints were really invaluable. He attributed great importance to a reasonable geometry of proposed structures, but the criterion of their soundness was, of course, the satisfactory agreement of calculated and observed F values. Since no computers were available at that time, far fewer reflexions were used for a structure determination, which was then somewhat of an art rather than pure logic. Still, all structures determined at Manchester are valid today, with more or less refined parameters.

Pretty models were prepared of the newly determined structures and Bragg showed them with great pleasure to every co-worker.

I learned the technique of oscillation diagrams on staurolite, a silicate of complicated composition, which is a minor constituent of several volcanic rocks. I made the necessary diagrams within one month and I learned how to assign indices to the reflexion spots by the method of Bernal. The space group $D_{2h}^{17}-Cmcm$, reported by Cardoso, was confirmed, and with the aid of J. West I began measurements of absolute intensities on a crystal of nearly 2 cm, obtained from the Manchester Museum. The series 110 and 111 were measured on natural faces, but the faces (100) and (001) had to be ground on the crystal. The famous ionization spectrometer of W. H. Bragg gave excellent intensities – of course with a little more work than the modern single-crystal diffractometers – from which absolute F values could be calculated.

After obtaining the F values of the reflexions of the 100, 001, 110 and 111 series I proceeded before Christmas to the structure determination. One had a clue from the axial lengths that oxygen ions were in cubic closest arrangement in staurolite, which was a close packed structure after Bragg & West. The base-centred orthorhombic symmetry of the lattice allowed only a few different oxygen atom arrangements and cations could be placed in the tetrahedral and octahedral interstices of the oxygen (and hydroxyl) ions. It was known that Si is tetrahedrally coordinated and one assumed independent SiO_4 groups. In this way I was able to enumerate all possible cation arrangements and compare the measured absolute F values and the visually estimated intensities of my films with those calculated from the structure.

Structure determination was accomplished on the second day of Christmas and when I showed it to Bragg next day, he approved it, to my great pleasure.

This determination was based on an ideal chemical formula $2\text{Al}_2\text{SiO}_5 \cdot \text{Fe}(\text{OH})_2$, deduced by me, which was not exactly in accord with the only good analysis available then. The formula suggested that parallel layers of the composition Al_2SiO_5 and $\text{Fe}(\text{OH})_2$ were present. We found, with W. H. Taylor, that the structure of the Al_2SiO_5 part of staurolite was somewhat different from the formerly published structure of kyanite. The new coordinates of kyanite derived from the positions of Al, Si and O atoms in staurolite gave very satisfactory agreement with the experimental intensities of the reflexions from this crystal. Recent refinement of the kyanite structure by Burnham (1963) confirmed our structure. So the structure determination of a complicated crystal gave the structure of another crystal, contained in the lattice of the former.

When the real chemical formula of staurolite was established by mineralogists, we were able, (Náray-Szabó & Sasvári, 1958) to uphold the original structure with a modification of the composition of the hydroxide layer; quite recently the staurolite structure has been refined by J. V. Smith (1968) with the most modern measuring and calculating facilities – unfortunately not available to me. The principles of our structure have been affirmed with some modification of the parameters of the ions and of some ‘occupancies’.

Although J. V. Smith used thousands of reflexions and the best possible facilities, some lesser details are still unsettled and as he writes in the first and last words of his paper: ‘Staurolite has been ... (and)

remains an enigma.' But the knowledge of nature's objects will never be final and unchangeable.

During my two years at Manchester many other silicate structures became known through the work of W. L. Bragg and his colleagues. The foundations of the system of silicates came to light through the efforts of the Manchester school, and Bragg's fundamental summarizing paper *The Structure of Silicates* appeared in 1930. By this work silicate science, which up to that time relied on transient hypotheses only, obtained a sound experimental basis. Of course, a great deal of further research has since been carried out elsewhere and great a number of new silicate types have been determined. None of these are in contradiction to the basic principles propounded by Bragg. The exceptional theoretical and practical importance of the silicates makes his achievements exceedingly valuable.

I determined at Manchester also the structures of apatite and apophyllite (the latter with W. H. Taylor), but I did not succeed with epidote. I also witnessed many important silicate and other structure determinations: danburite by Machatschki & Dunbar, KH_2PO_4 by West, the mica muscovite by West & Jackson, andalusite, sillimanite and analcite by W. H. Taylor, titanite, benitoite, thortveitite and hambergite, further KClO_3 by Zachariasen, and Na_2SO_3 by Zachariasen & Buckley.

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W. L. Bragg – An Appreciation

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I was fortunate in being associated with Sir Lawrence Bragg for about fifteen years. In the early 30's Beever and I used to come over from Liverpool to Manchester to seek his advice, which was always freely given. Later, he obtained a grant for me to work in his department and when he became Director of the National Physical Laboratory he invited me to accompany him to continue my work there; this was my first proper post. When he succeeded Rutherford as Cavendish Professor at Cambridge in 1938, he had me appointed to an assistantship there and I stayed in this position until the end of World War II. I was, therefore, exposed to his methods and ideas over a considerable range of activity.

His outstanding quality was – and still is – his ability to see the essential point of a problem and to strip away the inessentials. It was this quality that enabled him to dispense with the mathematical formality of Laue's theory of X-ray diffraction by a crystal and to substitute for it the simple effective law that goes

The determination of many silicate structures and the silicate system of Bragg showed in a great number of instances, how greatly the application of X-rays may promote chemical research. Later on the structures of many other important groups of inorganic compounds were elucidated by X-rays, such as the structures of sulphates, selenates, tellurates, phosphates, arsenates, antimonates, germanates, borates *etc.* By these researches unknown domains of inorganic chemistry were opened. This process has been continuous and is still going on; X-rays are an indispensable tool of modern inorganic chemical research.

On my return to Hungary I resumed my X-ray diffraction work at Szeged and later in Budapest and determined with my co-workers a number of new structure types.

Being one of the oldest crystal structure workers I often recall, and always with pleasure, the happy years at Manchester under the so friendly and inspiring guidance of W. L. Bragg and I hope he will be able to continue his splendid work for many years to come.

References

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by his name and which is still the central theme of the subject. It was this quality that enabled him to work out the first crystal structures, and then to tackle the much more complicated structures of the silicates – work that was coming to its end when I joined his department in 1936.

I was awarded a grant to work under A. J. Bradley on metal structures. At the time, flushed with the success that Beever and I had had with the use of Fourier methods in the determination of the structure of copper sulphate and the alums, I must admit that I was disappointed at having to switch my mind to what appeared to be the relatively simple problems of metal structures. But Bragg had decided that metals and alloys were the next main field in physics to which the new techniques should be applied, and I can now see that he was right. I am sure that I learned much more physics from this new field than I would have done by continuing to work with structures of inorganic hydrates.