Schools and Regional Development

CHAPTER 17

British and Commonwealth Schools of Crystallography

17.1. GENERAL SURVEY

by J. D. Bernal

The position of the British schools in the history of the development of our subject is necessarily quite a special one. Not only did Sir William and Sir Lawrence Bragg effectively start the study of crystalline structures by means of X-ray diffraction, but for many years their respective schools at the Royal Institution and in Manchester were the centres of world study in these fields. Naturally, important centres in other countries existed from the start and we have records of them in the succeeding chapters, but the primacy of the British schools was recognized, at the outset, by the large number of visits of young crystallographers, who were destined later to become the centres of schools of their own in other countries. Owing largely to the personal character of its founders the development of crystallography had,

from the very outset, a peculiarly intimate and friendly character. All of those who worked at the Royal Institution or in Manchester carried away for the rest of their lives recollection of the atmosphere of active and exciting research which grew up around the Braggs, and the fact that they were father and son actually helped enormously to unify the whole subject.

.To attempt adequately to deal in a few pages with the growing and diversifying field of structural crystallography over a whole of fifty years would be an impossible task. What we have chosen to do is to select the two principal schools, those of the Royal Institution and Manchester University, on which we have the detailed accounts of Professor Lonsdale and Professor James, each associated from the beginning with these schools and contributing greatly to them, and to add a necessarily more summary sketch by Professor Bernal of the other schools in Britain and the Commonwealth which in almost every case arose directly out of them.

To do this, the most arbitrary but, at the same time, necessary simplification is to attempt to divide the period into sections. It would be very convenient to take them as the first, second, third, fourth and fifth decade, but it did not come out quite like that because of the intervention of two World Wars. So we have first a short and intensely brilliant period beginning with the work of Sir William and Sir Lawrence Bragg on the simple salts, and corresponding work by Darwin and others on the theory and corrections of X-ray diffraction by crystals. This work was, effectively, broken off by the war. The second period may be reckoned from 1919 when Sir Lawrence Bragg went to Manchester or from 1923 when Sir William started work at the Royal Institution Davy-Faraday Laboratory. It may be considered to last until about 1929 when some of the first research workers from these laboratories set out and started schools of their own, notably in Cambridge and Leeds. This leads to the third period from 1929 to the beginning of the Second World War which had a large proliferation of schools, particularly in Leeds, Birmingham, Oxford and a further development in Cambridge and many other centres, a period which, effectively, came to an end with the transference of Sir Lawrence Bragg to the Cambridge Chair after Rutherford's death in 1937. Though the second war interrupted research, the period cannot in this case be passed over as such a blank in crystallography in Britain as was the first. Some very interesting work was done on structures of various explosive compounds, and the end of the war marked one of the great triumphs of crystallo-chemical chemical research, the elucidation of the

structure of penicillin. The fourth and last period we may take as that which we are now in, although it might be possible to divide it into two with the line somewhere about 1957 when the influence of electronic machines was fully felt, and where such elaborate structures as vitamin B_{12} marked the high-water mark of the analysis of non-protein biological structures. However, here no attempt at this division will be made and the whole of the latest or modern period will be treated as one.

Another division which is, in a sense, imposed by the nature of the subject itself, is that between the different fields of study. There has been a continuous interaction between the *subjects* of crystalline materials studied on the one hand, and the *methods* used for interpreting them on the other. This is not an attempt to give a history of either of these aspects of research in Britain—for the world as a whole they are given elsewhere in this volume. Here they can only be alluded to in passing where the particularly important landmarks occur. But the division according to fields of study follow much more closely that of the different schools with which we are concerned here.

From the very outset there was an almost tacitly agreed separation between the work of Sir William and Sir Lawrence Bragg, that is between the Royal Institution and Manchester, corresponding to that between organic and inorganic chemistry. With the one important exception of crystalline forms of silica, Sir William's laboratory occupied itself with organic crystals and Sir Lawrence's with minerals and metals. In Britain and the Commonwealth the latter two fields of interest remained linked although, in fact, they corresponded to different methods of study, the metals in particular leading to refinements in powder diffraction techniques.

As further schools developed, and largely on account of whether their leader came from London or Manchester, very much the same specializations were carried over and when we speak of the schools we generally speak of bodies of research workers occupied in elaborating some particular field of work; this was often even more specialized such, for instance, as that of Astbury, starting in the Royal Institution and going on at Leeds, which was centered on the study of fibres and particularly fibrous proteins and nucleic acids.

When we look at the actual lines of development, we see very clearly that they depended on the possibilities available to the original founder, to get the necessary support and interest in his work. Those who were successful in achieving the professorial chair in a fairly large university were able to set up large schools which proliferated into

many other places. Those, on the other hand, who occupied relatively subordinate positions in physics or chemistry departments, remained, for the most part, as isolated research workers or having one or two students at a time, and though the work they did was of the highest quality, it can hardly be said that they founded a school. This is brought out very clearly also by the way in which the transfer of an individual research worker from one university to another could result not only in the setting up of a new school in the second university, but often in the disappearance of crystallography altogether from the first. What we see, accordingly, is a fluctuating pattern lit up for a few years by the presence of a research director with drive for the time of his tenure there.

As it is a young subject, we crystallographers are still in the happy position of having with us many, indeed most, of the second generation of workers and one of the first, Sir Lawrence himself. The subject is still, in Britain, in a state of rapid growth and differentiation. We can only touch here on some aspects of the spread outside the field of fundamental science, that is, into industry and government service, although, in fact, in crystallography, industry contributed many elements to the fundamental study of crystals themselves, notably in the analysis of penicillin.

One conclusion is very evident, namely, that the development of this subject was a matter in which general or conscious planning had extraordinary little to do. Only in one or two cases, notably in Cambridge, did the University, itself, decide that it must have a crystallographic department, but in most cases, crystallography occurred almost unintentionally when a Chair of Physics or Chemistry happened to be awarded to a crystallographer as the most distinguished available candidate in a field which covered all branches of the subject. The non-establishment of chairs of crystallography in Great Britain has prevented the continuity which could so easily have been ensured in view of the availability of men of quite exceptional enterprise. There is no doubt that crystallography at several stages in its development in Britain was such an attractive subject that it automatically selected such people and the fact that a relatively unknown subject could acquire, in such a short time, no less than seven Fellows of the Royal Society, is some indication of it.

In a survey like this it is clearly impossible to be comprehensive. There are literally hundreds, the actual figure is around 820, of active crystallographers in Britain and the Commonwealth today. They cannot all, or even any large portion of them, be mentioned here by

name as this would reduce this report to a mere catalogue. It is inevitable that the omissions may create the impression of invidious selection but all one can do is to use one's own judgment to pick out those who seem to have been able to contribute definitely new directions to the study of the subject.

THE FIRST DECADE

In the first and glorious three years from 1912 to 1914, the study of the new-born subject, crystal structure and X-ray diffraction was necessarily limited to Cambridge and Leeds, the places where the Braggs were working, and to one other centre of vital importance, namely Manchester, in which the chair of physics was occupied by Rutherford then at his most creative time. This is the period culminating in the classic book *X-rays and Crystal Structure*, published in 1915.

The story of this period in Manchester is briefly told in Professor James' article. It must be emphasized that the work of Moseley and Darwin not only laid the foundations for the study of X-ray spectra and the principles of X-ray diffraction, but also included what is only now realized to be the important study of crystal imperfection, involving mosaic structure and primary and secondary extinction. In addition, and quite outside the fields of crystallography, the diffraction of X-rays by crystals furnished absolutely vital elements in the building up of the Rutherford-Bohr theory of the atom. It was in this period, too, particularly in Leeds and Cambridge, that the basic equipment for X-ray analysis was developed. The ionization spectrometer, with which much of the early work was done, was a product of earlier studies of nuclear radiations, an adaptation to the use of X-rays of Bragg's former study of the ionization produced by alpha particles. The photographic method also arose from the needs of X-ray spectroscopy as used by Moseley.

One other figure belongs to this early period and that is the veteran of crystallography, Professor Owen of Bangor, who in Richmond in 1913 started the study of metal structures in Britain which he subsequently carried out at Bangor. There was an even earlier influence, emanating from Edinburgh with Barkla, who had carried out the pioneer absorption measurements which had distinguished the K-, L- and M-levels of X-radiation. Unfortunately, his attachment to the non-existent J-radiation prevented him in his later days from making a serious contribution to the new diffraction crystallography. But some of his students started schools of their own, notably R. T. Dunbar at Cardiff.

THE SECOND DECADE

After the end of the First World War, that is, effectively in 1919 when Sir Lawrence Bragg took up his chair at Manchester to which he had been appointed in 1915, a new start was made and the corresponding transfer of Sir William, first to University College in 1919 and then to the Royal Institution in 1923, ensured the foundations by the beginning of the twenties of powerful new schools of structure analysis who set themselves to the essential task of working out the basic types of structure of solid substances, beginning very rationally with the simplest, the elements and simple salts. It is astonishing to think that, in fact, by putting together the pre-war and immediate post-war work, all the major types of structures known to us now had been studied in at least one example and essentially the right structures attributed to them. Most of the work in this decade is reported on here in the sections of Mrs. Lonsdale and Professor James because at that time the Royal Institution and Manchester schools effectively dominated structural studies in Britain. There were, however, important other elements which were just coming into play at this time. The old schools of crystallography of Oxford and Cambridge were still in vigorous life and it was owing to the inspiration of Dr. (and later Professor) Hutchinson at Cambridge and Professor Bowman and Dr. Barker at Oxford that the new methods were introduced. Dr. Wooster at Cambridge and Mr. Powell at Oxford were, in fact, the first X-ray crystallographers who had not been trained in the Manchester or Royal Institution schools. Another new school appeared at Bristol in the work of Dr. Piper on long-chain compounds which was to link up with those of Müller and Shearer at the Royal Institution and lead to the first effective break-through into the study of organic chemistry by X-ray methods.

The study of X-ray spectra was carried on with the original inspiration of Barkla by Professor Dunbar at Cardiff, followed by Professor Robinson. The corresponding study of absorption spectra with their implications on the theory of metals was particularly studied by Dr. Skinner at Bristol. However, it must be admitted that comparatively Britain has contributed little to the study of X-ray spectra.

THE THIRD DECADE

The years 1927–29 were to see the dispersal of the original schools and the start of the new ones. Bernal went to Cambridge, Astbury to Leeds, and Cox to Birmingham. The middle of the thirties was to see powerful schools of crystallography set up in Cambridge, Oxford, Leeds,

Birmingham, Liverpool and Bristol. Something can now be said about the individual character of these different schools.

Cambridge

The Cambridge school, in accordance with its tradition, for Bernal had been trained in classical crystallography by Professor Hutchinson, occupied itself with extensive studies in different fields of crystallography, both inorganic, including metals, and organic. From 1933 onwards the emphasis was on the organic side, corresponding to a division of the school between the Cavendish Laboratory on the one hand and the new Mineralogical Laboratory, which under W. A. Wooster devoted itself very largely to crystal physics and to the development of X-ray equipment and accurate intensity measurement. The study of metals in Cambridge, after a systematic start by Bernal, lapsed until it was again taken up by W. H. Taylor in the subsequent decade, but work went on very actively in the fields of inorganic compounds following the stimulus of the new Goldschmidt views of crystal chemistry and particularly in the study of water and hydroxyl compounds with Dr. Megaw. Here the link with the Cavendish was emphasized in the paper by Fowler and Bernal in 1933 on the structure of water and ionic compounds. This work was to form the structural basis for the understanding of hydroxides and hydrogen bonds.

At the same time in close connection with the Biochemical Laboratory of Professor Hopkins, work was started, first on amino acids and then on the sterols. There, owing to what was effectively a happy chance of being able to discover, by X-rays in the first place, the correct carbon skeleton of the sterols, Bernal was able to unify the structure of these important bodies which were then of particular interest in connection with vitamins and sex hormones. It was at this point that Miss D. Crowfoot (Mrs. Hodgkin) joined the laboratory and immediately became involved in both extensive and intensive structure work on the sterol compounds which was to lead later on to her great achievements in other organic fields. In 1934 the first successful photographs were taken of protein single-crystals due to a tactical break-through of examining them in the wet state. Miss Crowfoot continued her work with insulin in Oxford and the continuation of the sterol work was taken over by I. Fankuchen who had joined the laboratory from Manchester and originated from the United States. In 1935 Max Perutz came to the laboratory from Mark's laboratory in Vienna and started the studies of the haemoglobin systems which have now become classic. In 1936 another break-through was made in the

examination of the structure of crystalline and paracrystalline viruses, in the first place of tobacco mosaic virus prepared by Bawden and Pirie. This led, in the first stages, to the use of very small angle scattering in order to elucidate the intermolecular structures of the liquid crystal aggregates formed in these viruses and incidentally to an understanding of long-range forces between colloidal molecules in solutes. The significance of the high-angle reflections which indicated something of the internal structure was, however, not worked out until much later, largely by Miss Franklin. Fankuchen also continued this work with Bernal after the latter's transfer in 1938 to the Chair of Physics at Birkbeck College, London, for the few months that elapsed before the beginning of the Second World War. During the same period Professor Ewald left Germany and joined the crystallographic laboratory where his influence was very large, incidentally, in setting up the discussion group known as the Space Group.

Oxford

Unlike the other schools mentioned, where the initiative had primarily come from physicists, in Oxford the impetus for crystal studies was that of chemical crystallography originating with Myers and with Barker who had been a friend of Fedorov. X-ray studies began with the appointment in 1929 of Mr. H. M. Powell as demonstrator of chemical crystallography. Powell's earlier work was largely with coordination complexes. The further developments of his work and his discovery and study of clathrate compounds followed naturally from this. His first student was Miss Crowfoot who worked with him on a thallium metal complex. She returned from Cambridge to the department in 1934 and went on there with her work on the analysis of complex organic compounds of the sterol type, particularly the structure of cholesterol iodide with Dr. Carlisle, while following her studies of insulin and lactoglobulin. Powell continued, now with A. F. Wells, on the structure of further complex compounds including the carbonyls and phosphorus pentachloride; the latter was proved to be an ionic compound in the solid state.

An entirely independent research section at Oxford was that of Metallurgy which was taken over by Hume-Rothery following on the work of the Swedish school and of Bradley. This led to the interpretation of the so-called alloy phase systems, particularly of the A and B group metals, which he has continued with his students ever since. The Hume-Rothery rules, which laid the foundation for the idea of electron compounds, were the first fruit of his work.

Birmingham

The beginning of modern crystallography at Birmingham came with the invitation in 1929 by Professor Howarth for Cox from the Royal Institution to set up a study of the constitution of the sugars. This problem, with the methods of the time, proved too difficult and Cox very wisely elected to apply an indirect approach and, with the help of Goodwin and Llewellyn, worked out the structure of pentaerythritol which was to turn out to have the most interesting physico-crystallographic properties. It was also an early example of three-dimensional Fourier analysis of an organic crystal structure. At the same time, he studied the structure of ascorbic acid—vitamin C—as well as glucosamine hydrochloride, the first optically active organic substance whose structure was determined by X-ray analysis alone using the ionic replacement method. Through this he established the stereochemistry of the pyranose rings in sugars. A number of inorganic coordination compounds were also studied. At this time Birmingham was one of the most fertile centres of X-ray analysis but most of this activity was switched to Leeds when Cox became the Professor of Inorganic Chemistry there in 1945.

Leeds

Already in the thirties, however, Leeds had become an important centre of structural studies with, in the first place, a bias towards those of biological origin and particularly of fibres. Very appropriately, Astbury had been invited to a lectureship in textile physics and immediately started his classical work on wool and other fibrous substances. Beginning in 1929, he established the fundamental character of the alpha-(coiled) and beta-(straight) configurations of wool and showed that they could be extended to cover most types of protein fibres, though collagen represented an exception. This new type of analysis brought X-ray crystallography for the first time in contact with the morphological and histological aspects of biology. Hitherto it had been limited to the biochemical aspects.

Another line of research opened in Leeds when in 1935 G. W. Brindley joined the Chemistry Department. There he developed accurate powder photography and developed the appropriate cameras, laying the foundation for future work on the structure of clay minerals which he was to continue in the next decade.

Liverpool

A small school existed at Liverpool consisting of Lipson and Beevers as mentioned in Professor James' article. Until they moved to Manchester in 1936 their work on the structure of salts might be considered as a part of that school.

Bristol

The crystallographic school at Bristol, under S. H. Piper, remained during this period an active but highly specialized one concerned, very largely, with the study of fatty acids and waxes of natural origin and their derivatives, ketones, secondary alcohols and other constituents.

Commonwealth Schools

The decade of the thirties also saw the beginning of X-ray work, generally inspired from the older centres, in India with Banerjee in Calcutta, and Krishnan at Bangalore, where a very interesting field of relations between the structure and the magnetic properties of crystals was first explored. It began then, too, in Canada with Barnes at Montreal and in South Africa with Professor James at Cape Town.

This completes a rapid survey of the major schools of crystallo-graphic research in Britain and the Commonwealth in the decade before the war. It was a period of extremely happy activity over rapidly broadening fields. To sum up, the effect was to establish the approximate structures of most types of crystalline materials with a degree of accuracy and refinement which, though it would naturally not now be considered adequate, was quite sufficient in those pioneer days for establishing some of the major features of molecules, particu-larly in the organic field, and of the ways of linking them together. The concept of hydrogen bonding added to those of Van der Waals, and ionic linkage also appeared. At the same time the major structural types of the inorganic world, the fibrous and platy silicates, were worked out and a beginning made in the understanding of the rules of compound formation in the far more complex field of alloy structures. Effectively, this marked the creation of two new subjects, mineral chemistry and alloy chemistry, as rational disciplines, a task that had proved impossible and would probably have long continued to be so without crystal analysis.

17.2. CRYSTALLOGRAPHY IN BRITAIN DURING AND AFTER WORLD WAR II

by J. D. Bernal

Unlike the period of the First World War which marked a virtual cessation of structural crystallographic studies in Britain, the Second World War was one of considerable if limited activity closely linked with the needs of the war itself. It was marked by the greatest triumph of crystallographic technique that had yet occurred, namely, the elucidation, essentially by X-ray crystallographic methods, of the structure of penicillin. The story cannot be told here, but this achievement is a remarkable instance of the way in which research can be pushed forward if it is led by workers of genius backed by keen young collaborators. The molecule of penicillin was one of peculiar intractability by purely chemical means on account of its thiazolidine-β lactam ring system, so that knowledge of the molecular structure was essentially gained by X-ray analysis. Though the ultimate objective, a simple non-biological synthesis of penicillin, was not achieved until 1958, this is no reflection on the methods of analysis the results of which the final synthesis fully justified. The work is of interest from another point of view, as an example of fruitful co-operative research. Two groups, at Oxford and at the Northwich Division of the I.C.I., led by Dorothy Hodgkin and Bunn respectively working closely together on different varieties of crystals, were able to supplement each other's work. It was a magnificent start to a new era in crystallography.

These are not the only achievements of war-time crystallography. Some very interesting analyses of explosive substances were carried out under Cox at Leeds, leading to the understanding of the structures of nitrate groups and strong acids; and everywhere crystallographic methods were used for general auxiliary and identification purposes as well as in the study of metals and alloys. Everything was ready for a new burst of activity as soon as the war was over. However, there was one tragic loss, that of one of the founders of the subject. Sir William Bragg, who was still in his full mental vigour, and actively directing the Royal Institution laboratories died in January 1942. His last researches dealt with the pioneer field of the non-Bragg or diffuse reflections of X-rays. With him passed the first generation of X-ray crystallography, but fortunately his son, as inseparably linked with the original discovery, is still with us.

POST-WAR PERIOD, 1946–1962

After the end of the war, the expected new start of crystallographic research exceeded all expectations. War service released an augmented band of crystallographers including part of the second and now the beginning of the third generation of crystallographers, those taught by Bragg and those taught by his immediate pupils. All the old schools of crystallography renewed and multiplied their activities and new ones were founded in practically every university in England, Scotland and Wales.

During the war period and to an increasing extent after it, Britain had ceased to be the rather isolated centre of structural research and became part of an ever closer linked international exchange of persons and problems and materials. The formal side of this, the foundation of the International Union of Crystallography, is accounted for in another chapter, but here it can be said that world crystallography had grown, not only in extent, but in intimacy of cooperation during the whole period.

The characteristic of post-war work in crystallography in Britain has been the enormous increase, both in scope and in quality of the work, brought about by the new problems and the new methods. The much more critical understanding of the methods of diffraction analysis, though they contain few radically new principles, has made it possible to tackle crystals with molecules of enormous complexity up to the proteins and to a certain degree of far larger molecules like those of the viruses. At the same time it also has enabled much more precise information on structures to be obtained of crystals with relatively small molecules. These later developments would have been impossible without the increasing use of ever faster electronic machines, beginning effectively in 1957, and this latter period might even be called the first computer age of crystallography.

At the same time, the developments in theories of chemistry have given a much greater importance to the precise knowledge of structures, and the developments of theoretical chemistry in the hands of such pioneers as Coulson, Dunitz and Orgel have led to a new link between crystallography and organic as well as inorganic chemistry, including the intermediate field of organic metallic complexes.

A definite break into new ground came with the realization that the methods of diffraction could be applied with precision to structures without three-dimensional lattices, using in the place of the methods of Fourier analyses those of Bessel functions. This development was called for in the first place through the study of protein fibres but it was

rapidly extended and deepened in the analysis of viruses and other irregular structures such as those of liquids. This was to lead to one of the greatest triumphs of crystallography in the biological field, the structures of nucleic acids, of which the pioneering work had been done long before by Astbury.

Cambridge

The transfer of Sir Lawrence Bragg from Manchester to Cambridge had occurred too shortly before the war to make a notable impact there until after the war but then crystallographic work began with redoubled vigour. The main strength of the Manchester school was soon effectively transferred to Cambridge where two closely linked groups of research workers grew up in the post-war years. One of these, representing a fusion between the Bragg and the Bernal schools there, developed the studies on organic crystals and proteins. On the other, the inorganic side, W. H. Taylor took over in 1945 the direction of the main laboratory and continued his work mainly on metal structures.

In the atmosphere of Cambridge, the metallographic side of the work developed in new directions. P. B. Hirsch, in particular, used micro X-ray beam methods to study dislocations and also imperfect crystallization in close connection with the electron microscope developments which were going on there under Coslett. Thus, the earlier Cambridge work of G. I. Taylor and Elam on metal deformation was blended with that of W. L. Bragg at Manchester. With Miss Megaw transferred from the Birkbeck team, they continued the work on silicate structures but particularly on the most intractable of the types of rock mineral structure, those of the felspars and, also, of hydrated calcium silicate compounds connected with cement, following up the work which was also being carried on by H. F. W. Taylor at Birkbeck. Miss Megaw has also, through her studies of the titanates, made notable contributions to the theories of ferroelectricity.

During the same period, the possibility of the use of electronic computing machines increased and the advantages of Cambridge were manifest in the brilliant work of Cochran in developing precise methods of crystal analysis applied in the first place to organic crystals but of perfectly general applicability. It was largely Cochran, in his very critical approach to crystal structure work, who raised the standard of over-all accuracy and in particular of bond length determinations by something like a factor of ten, but at the same time inevitably increased the amount of work that had to be done to determine the crystal structure properly. This, effectively, led to a division of the subject

between rough analyses useful to the chemist from the point of view of determination of the main lines of structure, to the precise analysis now being required to check studies of theoretical chemistry.

Sir Lawrence Bragg, on moving to Cambridge, had taken over not only his own metal and silicate school, but the organic and bio-molecular school which had been built up in Cambridge by Bernal. This, however, remained somewhat separate from the other group, partly for administrative reasons because it had acquired the support of the Medical Research Council; Perutz's researches on haemoglobins were continued on an ever expanding scale. Soon after the war, he was joined by Kendrew and a number of other fellow workers and between them they carried out the magnificent and ultimately successful attack on the structure of the haemoglobin and myoglobin crystals which were to result in the first strictly X-ray analysis of a protein structure. This, however, was not to be the only triumph of the school because, at the same time, one of the protein workers, Francis Crick together with Watson in the United States, put forward the hypothesis of the double spiral structure of nucleic acids, which was later to prove the clue to a fundamental understanding of biological structure and function, including the effective action of viruses, and a material explanation of genetic processes. The development itself is an example of international cooperation, the final proof by more careful X-ray analysis being left to another school, that of King's College in London with the work of Wilkins, Goodwin and Miss Franklin.

Another branch of crystallographic work at Cambridge was in the department of Mineralogy where Dr. W. A. Wooster continued to direct the only undergraduate courses on Crystallography given in Britain. His own researches now concentrated on the quantitative study of diffuse X-ray reflections, from which to determine elastic constants of crystals. This led, in conjunction with the work of Laval, to criticism of the long established theories of the relations of crystal elasticity to symmetry.

The London Schools

The Royal Institution. When in 1954 Professor Bragg retired from the Cavendish Chair at Cambridge, and moved to the Directorship of the Royal Institution which his father had held for many years, he carried with him in close cooperation with the Cambridge school some of the study of the proteins related to haemoglobin, and, as co-workers Dr. Green and Miss Scouloudi who had been attached to the Birkbeck school. Dr. Arndt at the new Royal Institution school has developed

also very powerful X-ray tubes essential for the study of the most complicated proteins and viruses.

Birkbeck College. J. D. Bernal came to occupy the Physics Chair at Birkbeck College too shortly before the war for it to have had much effect at the time. The physical destruction of the college in the London raids resulted in a delay in setting up work again after the war. However, by 1947 a new school of crystallography had definitely been established in some ruined houses and was being gradually expanded in the years that followed. Postgraduate classes in Crystallography were started in Birkbeck in 1949 on a London intercollegiate basis. In research Birkbeck took over effectively part of the work of the Cambridge school with one important addition. Thanks to a grant from the Nuffield Foundation it was possible to set up a biomolecular unit concentrating largely on the structure of proteins and viruses.

Other organic structures were studied such as those of terpenes. More important, however, was the study of pyrimidene by Parry and of the nucleoside, cytosine, by the Norwegian research worker, Furberg, who was able to show that the planes of the pyrimidene molecules were arranged at right angles to the rings of the pentose sugars. This provided the essential clue for the idea of a helical structure of nucleic acid.

In the protein field, C. H. Carlisle concentrated mainly on the structure of the enzyme ribonuclease which was to prove a much more difficult problem for technical and structural reasons than was expected or was that of the haemoglobins. However, it seems to be approaching a definite conclusion.

The virus work hung fire for longer until it was taken up with great energy and success by the late Miss Franklin who was able to demonstrate, following the initial hypothesis of Watson, that the virus molecule possesses a helical structure, though not one corresponding to a single molecular chain, but rather to an aggregate of identical protein molecules, inside which are twined the molecules of ribosenucleic acid. The major success was the determination of the position of the ribosenucleic acid as a single helix in among the protein molecules forming the protective tube of the virus. In further work on the spherical viruses which was started just after the war with studies of bushy stunt and turnip yellow virus, A. Klug was able to prove that these, according to the hypothesis of Watson and Crick, consisted of polyhedral aggregates with the uncrystallographic symmetry of five-fold units. At this point the studies by X-rays became blended with those by the electron microscope.

The other field of research was initially of an industrial character but it led to very interesting scientific results. It was to determine the structure of cement and its hydration product, concrete. These studies were carried out largely by J. W. Jeffery, H. F. W. Taylor and their co-workers. They developed an ingenious combination of analysis of fine-grained products produced industrially, with structural studies of slow grown natural crystals of the same material. It turned out that the main hydration product of cement was an extremely rare hydrated silicate mineral called tobormorite whose structure was ultimately determined by Miss Megaw, one of the original members of the team who was later transfered to Cambridge. This work extended out to the discovery of a completely new series of silicate structures both un-hydrated and hydrated, based on more complicated rhythms than the simple alternation which Sir Lawrence Bragg had found in the predominantly magnesium silicates of the pyroxene types, opening a new chapter in silicate crystal chemistry. The major work for this was that of Mrs. Dornberger, one of the original Birkbeck group, and later of her collaborators in Berlin, especially Liebau, and also of Belov and Mamedov in the Soviet Union.

It was about the same time that A. L. Mackay joined the Birkbeck group and opened up, with D. R. Das Gupta, a study on iron oxides and hydroxides using the new methods of electron microscopy and diffraction developed by Grudemo and Gard. In this way they elucidated a hitherto extremely confused chapter of inorganic chemistry. Through the magnetic properties of these compounds, this research was brought into connection with new studies of paleogeo-magnetism which Professor Blackett was directing from Imperial College.

Professor Bernal, in the later years, has returned to his earlier interest in the structure of water and simple liquids by generalizing the model of a liquid to one formed by a random aggregate of spheres in contact. This he has been able to relate to the X-ray diffraction from regular to irregular structures.

King's College. Professor J. T. Randall, whose fame has been associated with the development of branches of physics, essential for the military successes in the war—luminescent materials and the magnetron valve —opened his new laboratory at King's College with a concentration on a very different field, that of biomolecular studies. Apart from the development of the electron microscope for these purposes, which does not come precisely into our field of concern, M. H. F. Wilkins began

there with the study by X-rays of natural polymers with helical structure. One of these was the anomalous structural protein collagen, further studied by Miss Cowan and then by Ramachandran in Madras. Another was the vastly more important structure of the nucleic acids where Wilkins and his school, basing themselves on the Crick and Watson hypothesis, were able to verify the double helical structure and to produce the remarkable models which showed how this structure depended on the fit of a number of very closely packed groups of purines and sugars. The work of Randall and Wilkins definitely established biomolecular studies as a discipline of their own and, as a result, part of the new institute of biophysics attached to King's College is devoted entirely to this study.

*University College.** The revival of X-ray studies at University College came in 1946 when Kathleen Lonsdale, later Dame Kathleen Lonsdale, moved from her long held position at the Royal Institution to become Professor of Crystallography in the Department of Chemistry. This was particularly important from the point of view of teaching and research. In teaching for the first few years, she joined in an Intercollegiate Course which had been organized at Birkbeck College, and took part in the formation of the first generation of London students of crystallography. In her research she followed original lines, lying more in the development of crystal physics than crystal structure analysis. Some very interesting work was done by Dr. P. G. Owston on ice which much improved our knowledge of this really very complicated substance with special reference to the H positions. Professor Lonsdale's own chief contribution was to the study of the thermal vibrations of crystals. This was now becoming essential for structural analysis because refinement had reached such a stage that the movement of the atoms could no longer be neglected. However, she used this to study still further the peculiar anomalies in scattering in directions outside those predicted by Bragg's Law and which correspond to various irregularities, either intrinsic or thermally induced. She also continued her interest in the magnetic properties of crystals, linking them more quantitatively with the structure.

A separate school of work was on the subject of refinements in the structure of diamonds, now including artificial diamonds, carried out in conjunction with Miss Judith Grenville Wells (later Mrs. Milledge). The high standard of precision and of criticism in all this work puts it in the forefront of world crystal physical studies.

* See section 17.6 for the earlier work at University College, London.

Professor Lonsdale's school at University College has always had a particularly strong international character. Students from no less than twenty different countries, in all five continents of the world, studied there the methods she had developed and later several of them, having returned to their countries, were to found their own schools. Close association with Egypt and India were particularly fruitful.

Imperial College. Important crystal structural work started in Imperial College with the appointment in 1957 of A. R. Ubbelohde as Professor in the Department of Chemical Engineering and Technology. He continued there the work he had already started in the Royal Institution and added to it with the assistance of Dr. G. S. Parry. His particular interest lay in crystal transformations with temperature and the detailed study of phase changes, thermal expansion and molecular movement. This led to a further understanding of the nature of some thermodynamic transformations in solid systems which are not, as was previously thought, necessarily of a higher order but may depend on the linking and mutual strain of two forms above and below the transformation temperature. These studies necessitated the development of a number of X-ray cameras to be used at different temperature ranges, much extending the armoury of such instruments.

Oxford

The three main divisions of the Oxford school continued under the same direction that they had enjoyed before the war. Organic crystallography with particular reference to natural products was developed by Mrs. Hodgkin. Dr. Powell continued and extended his study of coordination and clathrates while Dr. Hume Rothery systematically extended his metal and alloy studies.

Mrs. Hodgkin and her team, in close cooperation with others in America, particularly with K. Trueblood and J. G. White, carried out successfully the determination of the structure of the most complex molecule known at the time. It was one of extreme biological interest, the anti-factor for pernicious anaemia, so-called vitamin B_{12}. This analysis has become a classic. This is partly on account of the interest of the structure itself, which is an extremely complex unit including both proteinoid and neucleotide elements with a central reduced porphyrinoid group containing cobalt, and linked in a most unexpected way. But the analysis was also of great significance on account of the elaborate and critically accurate methods applied. Great use was made of machines in America and in Britain (Man-

chester, Leeds and National Physical Laboratory). Ninety-three atoms not counting Hydrogens were placed one by one ending in 1959 with the positioning of all the twenty-two water molecules in the structure. The method of analysis so successfully used was one which gave great hope to other crystal analysts, yet there was hardly any structure short of the proteins that could not be tackled by strictly crystallographic methods, that is by methods which did not involve any chemical assumptions. The results of such analysis are already of value to chemists and are likely to be of increasing use to them in the future. It seems extremely unlikely that the structure of vitamin B_{12} could ever have been discovered by purely chemical methods. The structure of penicillin might have been, but was not actually done in time. But with vitamin B_{12} the difficulties of the analysis were proving too great with the older methods. It would be wrong, however, to oppose X-ray to traditional chemical analysis. The two must work closely together especially on the most difficult cases. For instance, in the process of X-ray analysis of B_{12} studies were made of a number of its chemical derivatives which assisted very much in arriving at the final structure.

In 1960 Dr. Hodgkin was chosen as special Wolfson Research Professor of the Royal Society.

Dr. H. M. Powell, now Reader in Chemical Crystallography, continued to devote himself more particularly to the structure of molecular compounds. A certain number of straightforward molecular compounds, addition compounds such as those of aromatic polynitro compounds and other aromatic substances, had been studied just before the war. The real break-through came with the study of clathrate compounds particularly those formed by quinols in which Powell and Palin were able to show the way in which the smaller in general non-polar molecules are caught in a kind of basket in which the meshes consist of hydrogen bonded molecules. This includes even such normally completely unreactive molecules as the atoms of the rare gases. Powell's chemical interests led him further into the discovery of a new type of clathrate compound where the optical activity resides in the structure and not in the optical activity of the resulting molecules. Clathrates formed of this type which are analogous to those of right or left quartz or of benzil, have naturally a way of separating the right- and left-handed forms of smaller molecular species and thus are, in a sense, defying Pasteur's principle that optical antipodes can only be separated by substances derived from living structures including, as in his classical separation of optically active

crystals by hand of 1849, the living structure of Pasteur himself. In the case, however, tri-*o*-thymotide Powell was able to show that it is possible to separate a mixture of optical antipodes by methods involving neither biological products nor human intelligence, though the formation of the particular right- or left-handedness of the original clathrate crystal still depends on chance. Further work now going on is dealing with examples of ligands attached to particular inorganic ions. The laboratories of both Professor Powell and Mrs. Hodgkin were for a long time housed in the old Ruskin Natural History Museum in Oxford but since 1960 they have been moved to well-fitted and new laboratories in the chemical wing.

Dr. Hume Rothery and his school have continued their work on alloy systems of increasing range and complexity with the idea of arriving at a really quantitative alloy crystal chemistry. The later development of the studies has linked up the straightforward phase and structures analysis to the new considerations of dislocations, in particular to the immediate field of stacking faults and the study of the industrially enormously important martensitic transformations.

Leeds

In Leeds, after the war, the major lines of work of the vigorous Birmingham school previously described, were added to those already existing of Astbury's fibre structure work and of Brindley's studies on clays. The appointment of Dr. E. G. Cox to the Chair of Inorganic and Physical Chemistry in 1945, gave him opportunities to set up an even larger school than at Birmingham and the value of this has been proved by the work coming from it. Cox set himself essentially to study organic compounds of a relatively simple kind and to determine their structures with a very high level of accuracy. In this respect he and Robertson divided the field between them. While J. M. Robertson in Glasgow concentrated on aromatic compounds, Cox mostly concerned himself with aliphatic. With J. W. Jeffery he started the study of terpenes and other compounds related to isoprene. The structure of geranylamine hydrochloride is a landmark in structure analysis bringing out particularly the aspect of the variable heat motion of a chain attached at one end. The addition of D. W. J. Cruikshank to the team led to the introduction of rigour in the calculation which has helped very much in determining accurate bond lengths. Co-ordination compounds of stereochemical interest have been studied and further development of carbohydrates is under way.

This school has been particularly fertile in developing, not only

physical methods of examination, but also machines of an analogue or digital type; particular use was made of low-temperature methods to reduce the effect of thermal vibration and it is largely due to the Leeds school that three-dimensional analysis in Britain became almost *de rigeur*.

G. W. Brindley's work was, as already indicated, mainly concerned with clays but in the years after the war he developed this method further and was one of the leaders of the world study of clay minerals and their various streaks of hydration.

After the war, Astbury's laboratory, whose interests were turning more and more biological, was transferred from the textile physics department to a newly created one of biomolecular structures. Here he widened the scope of his studies from X-rays to electron microscopy and infra-red spectroscopy and extended it further to cover other groups of compounds, especially a group of fibrous proteins which had hitherto not been adequately recognized, the so-called crossed β structures and also the highly orientated natural protein structures, including such unusual things as the egg-case of the prying mantis or the peduncle of the egg of the lace wing fly. It was clear that before his last illness he was on the way to a kind of structural natural history of proteins which he was admirably suited to pursue.

Glasgow

The rise of Glasgow to being one of the major schools of crystallography followed the transfer of Dr. J. M. Robertson to the Chair of Chemistry. His stay at Sheffield, 1939–41, had been too short to enable him to set up a viable school there. One of the major achievements of the school is in its teaching capacity, for it has taken in people from many different parts of the world and the students have gone out to found other research laboratories very widely, including one in Europe, Dunitz in Zurich. Robertson had already established his special competence in the study of aromatic substances and particularly condensed ring compounds. He continued new refinements of these to meet the needs of theoretical chemists but went further to observe a number of related compounds of essentially aromatic character or of terpenoid character such as limonin, cedrelone and calycanthine. These are magnificent examples of the use of X-ray analysis for solving problems which are extremely difficult for purely chemical methods and Robertson's knowledge of chemistry as well as of crystallography stood him in good stead. He also gave an account of rings of unusual numbers, particularly those of azunine and tropolone. It was

largely due to Robertson's work that the idea of using X-ray crystal analysis has now spread widely in chemical circles and problems calling for them are very often sent to him or his students.

Manchester

In the University of Manchester physics department, the crystallographic work did not long survive the removal of W. L. Bragg to Cambridge where a number of his research workers joined him. However, one of them, H. Lipson was appointed Professor of Physics at the Manchester College of Science and Technology where he had been preceded by W. H. Taylor. He was soon able to set up there a small school of crystallography which was well able to carry on the Bragg tradition. He interested himself mainly in the methods of crystal analysis based on Fourier transforms and developed very beautiful optical representations which made the first stages of the analysis of many organic crystals almost an intuitive process. In this he was assisted by Dr. C. A. Taylor and others while Dr. M. M. Woolfson interested himself more in direct methods of analysis.

Bristol

The work of Piper on hydrocarbons, already mentioned, has been extended to artificial polymer hydrocarbons by Keller and has thus linked the work with that carried out in connection with the dislocation of crystal growth studies initiated by Professor Frank and the expression of his theory of spiral crystallization of substances. It is here, also, that the greatest concentration of work in connection with the physical properties, both electrical and magnetic, of ferro-electrics and ferro- and polar magnetics is being carried out. Resonance studies are fitted in with more precise knowledge of crystal structure of coordination complexes.

Cardiff

At Cardiff, under Prof. A. J. C. Wilson, another school of organic crystal chemistry has grown up, here concentrating on the alkaloids such as ephedrene to adharmine, and on a number of terpinoids such as longifolene. The research of Mr. Hine into amino acid derivatives led to the first determination of the stereoconfiguration of an optically active sulphur atom. Cardiff has thus become one of the leading schools of the refinement in organic crystal structure analysis. At the same time, much has been added to the theory, beginning with Wilson's enormously valuable method of determining the presence or

absence of the centre of symmetry by the statistics of intensities, and a critical appreciation of the value of analysis of crystals both perfect and imperfect. Most recently, Professor Wilson has entered the field of precise X-ray pattern determination in connection with the A.S.T.M. index and has raised the standard of accuracy of powder patterns to make them a far more precise method of identification than they had been hitherto.

Edinburgh

The transfer to Edinburgh of Dr. C. A. Beevers, who had already put crystallographers in his debt by his contribution to the Beevers and Lipson strips, started a school of crystallography there remarkable for its attack on the really difficult organic structures, those of strychnine and sucrose sodium bromide. It was here that Cochran, already mentioned, first started his X-ray work. Now the emphasis is still on sugars and their derivatives and alkaloids. Work is also being done on inorganic salts, particularly on the phosphates and sulphates.

Further British University Schools

Crystallographic work in *Belfast* was initiated by Professor Ubbelohde before he transferred to London in 1957 and, as already indicated, dealt largely with the study of crystal transformations, isotope effects and thermal vibrations. Miss Woodward, one of the original Royal Institution research workers, has particularly studied the whole range of transformations of single crystals of potassium nitrate. Though not directly concerned with analysis, the stay of P. P. Ewald in Belfast strengthened the interest there in crystallography especially on the optical and theoretical side.

Since the departure of Cox and Llewellyn, from *Birmingham* crystallographic work has not been on a very large scale but of admirable quality. Dr. R. W. H. Small's work on the effects of hydrogen bonds in sugars and other compounds was done here.

In *Dundee*, a small but flourishing school under Dr. J. Iball has concentrated on a group of important hydrocarbons of aromatic character closely associated with carcinogenic properties beginning with kerosine and 3,4 benzpyrene. The emphasis is on accurate determinations capable of explaining properties by anomalies in bond distances.

At *Newcastle* (Durham University), Dr. H. P. Stadler has been working on problems of interest to the properties and transformations of coal substances, particularly high complex fused ring hydrocarbons and

their derivatives. Work in the other parts of the University at Durham is being carried out by H. M. M. Shearer, especially on organometallic compounds.

Three new schools of crystallographic research deserve special mention. At *Keele*, North Staffordshire, the new University started in 1954 an X-ray crystallographic unit and Dr. S. C. Nyburg has been carrying out very interesting studies on inter-relations of organic structures which he has described in his book *Organic Crystal Chemistry*. At *Aberdeen*, H. F. W. Taylor, who transferred from Birkbeck in 1953, has continued work on silicates but made a welcome new approach by the use of a combination of electron microscopy and X-ray diffraction. Dr. Gard, who works with him in this field, has achieved the first analysis of X-ray structures by this method carried out in Britain. It was essentially a Russian and Swedish study hitherto (Pinsker, Vainshtein and Grudemo). A school of crystallography at *Nottingham* was set up in 1949 by Dr. Wallwork, formerly with Powell at Oxford. Its interests are in organic molecular complexes and anhydrous metal nitrates.

It can be seen that in practically every University in Great Britain, some research work in crystallography is being done and a certain amount of teaching is carried out. However, only in Cambridge for undergraduates and in Birkbeck College, London, for the M. Sc. degree, is the study entirely specialized. Elsewhere it is part of the general chemistry, physics or geology courses.

17.3. Post-war Commonwealth Development

by J. D. Bernal

Canada

The main centre for X-ray diffraction is in Ottawa at the National Research Council under Dr. W. H. Barnes (organic and inorganic structures) and Dr. W. B. Pearson (metals). Active research centres exist, however, at some of the Universities in the Departments of Geology and Chemistry. Of singular interest is the work done on neutron diffraction at the Chalk River reactor which, for many years, gave the highest neutron flux of all reactors. Considering the wealth of ores and wood, and the well developed metallurgical, pulp, and

other industries, it is not astonishing that they have introduced X-ray analysis, even though on a very cautious scale.

South Africa

Largely under the influence of Professor R. W. James, an interesting school of X-ray analysis was started in the early forties in the University of Cape Town. He, himself, completed there the second volume of *The Crystalline State*, that dealing with the principles of X-ray optics and diffraction.

The principal interest of the Cape Town School in which Dr. and Mrs. Saunder have been most prominent, has been in the structure of aromatic molecules and molecular compounds using three-dimensional methods and extending the analyses to cover cases of molecular disorder. It was here, also, that Dr. Klug began his studies on the use of Fourier transforms in crystal analysis, a study that has stood him in good stead in his later work on viruses.

Australia and New Zealand

The record of Oceania in post-war crystallography has been a distinguished one. An important and autonomous school of crystal analysis has been formed in Melbourne in the Division of Chemical Physics of the Commonwealth Scientific and Industrial Research Organisation (C.S.I.R.O.) under Dr. A. L. G. Rees. Here X-ray analysis is being combined with the development of electron microscopy and electron diffraction. The principal interest of the group directed by Dr. J. M. Cowley is the development of experimental techniques and the theoretical basis of the subject. In particular, methods have been developed for the structure analysis of submicroscopic crystals from single-crystal patterns obtained by using electron microprobe techniques, and a new formulation for the theory of electron diffraction and microscopy has been evolved.

In the X-ray group Dr. A. McL. Mathieson with Dr. J. Fridrichsons has carried out many structure analyses of moderately large molecules (20 to 50 atoms in asymmetric unit) including plant alkaloids and peptides, incorporating developments of low temperature, heavy atom and generalized projection methods. Dr. B. Dawson has concentrated on the super-refinement of more simple structure and the accurate theoretical and experimental determination of atomic scattering factors and their modification by ionization and bonding.

This school has already made its mark internationally particularly in generating new ideas and methods.

In another section of C.S.I.R.O., that of Tribophysics, work is directed by Dr. W. Boas, formerly one of the Berlin Dahlem group which laid the foundation of structural metal physics. The interest of present work here is largely directed towards the study of crystal defects and plasticity as affecting metals and to surface phenomena of catalyst crystals studied by electron diffraction and electron microscopy.

There has been a very interesting beginning of organic structural studies in the University of West Australia under Professor Birkett Clews and Dr. Marsden which has now been concentrated in Government laboratories. In Sydney H. C. Freeman, who received his training at the California Institute of Technology, is building up a school for organic structure analysis at the University of Sydney. Interesting structural work and research on metal textures is being carried out at two departments of the University of New South Wales.

The school of crystallography in New Zealand was initiated by Professor F. J. Llewellyn, formerly at Birmingham, at the University of Auckland in 1948. It has been largely concerned with the structure of nitrogenous organic compounds. After his resignation in 1956 it has been carried on by Dr. D. Hall. In 1954 another school has been set up under the direction of Dr. B. R. Penfold at the University of Canterbury working on inorganic crystals.

India

At the Indian Association for the Cultivation of Science, Calcutta, Professor Banerjee's school has continued and extended its work in post-war years. The main interest has now turned to the study of thermal diffuse reflections from organic crystals, as studied by R. K. Sen, S. C. Chakraborty and R. C. Srivastava in relation to the elastic constants. Studies have also been carried out by G. B. Mitra on coals and B. K. Banerjee on glass.

At the Indian Institute of Science, Bangalore, under the direction of R. S. Krishnan, work on diffuse reflections of X-rays has also continued. With G. N. Ramachandran detailed studies on properties of diamond have been made including thermal expansion and relation of mosaicity and luminescence. Studies have been carried out on coordination compounds and on complex organic crystal analysis, where several new methods have been developed including low-temperature and anomalous dispersion techniques, especially in the work of G. Kartha and S. Ramaseshan.

One of the most important contributions of the Indian school has

been the analysis of the structure of collagen as a three strand twined polypeptide, carried out by G. N. Ramachandran at the National Institute for Leather Research at Madras.

17.4. RESEARCH IN NON-INDUSTRIAL LABORATORIES OUTSIDE THE UNIVERSITIES AND THE ROYAL INSTITUTION

by J. D. Bernal

Although there are no institutes where a large part of the work is devoted to X-ray crystallography, valuable work and new initiatives have come in the field of crystallography from several governmental and independent institutions, ancillary to their main objectives. These can be classified, in general, according to the nature of the work. Those at the National Physical Laboratory and the Atomic Energy Research Establishment at Harwell have been concerned very largely with problems of metals, while those at the British Museum of Natural History, the Building Research Station, the Agricultural Research Stations at Rothamsted and Aberdeen, and the Safety in Mines Research Establishment in Sheffield have been mainly concerned with studies in minerals, the last three particularly with clays. In the National Institute for Medical Research and to a certain extent at Harwell, organic substances have been the centre of interest.

National Physical Laboratory
The contribution of the National Physical Laboratory began at the very outset of structural crystallography with the work of Dr. (afterwards Professor) E. A. Owen, of the Physics Division who, in 1923 and 1924, started the study of metal structures by the X-ray powder methods. These were among the first studies in metals by X-rays to be carried out anywhere. Afterwards he was joined by Dr. G. D. Preston and together they developed further some of the most interesting studies of age hardening and precipitation processes in copper aluminium alloys, which were eventually to culminate in the demonstration of the existence of minute copper-rich regions in an aluminium matrix. These precipitations, the Guinier-Preston Zones, coincided with the onset of hardening. Preston was also a pioneer in the use of precision parameter measurements. In 1926, the Laboratory

started a section on the application of X-ray methods to industrial research, some original members being H. M. M. Shearer, W. A. Wood and J. Thewlis.

Their main work was on phenomena concerned with the deformation of metals as well as the brittle fracture characteristics of iron. The value of this work was recognized in effect by the setting up of X-ray laboratories in many of the most important industrial firms so that the particular section was wound up after the Second World War and the whole of the X-ray work concentrated in the metallurgy division. Since the war the work has been continued on precipitation and binding processes but there has been also a condiderable development of X-ray techniques particularly in the direction of precision measurement.

Atomic Energy Research Establishment, Harwell

The work here is of two kinds, firstly that dealing with metals and other solids connected with the processes of atomic energy generation and secondly the use of neutrons for structural studies. The former part of the work concerns the properties of graphite, particularly very pure graphite, and studies, in particular by Kahn and Thewlis, on textural properties such as preferred orientation. Not only graphite itself but its reaction with other substances such as sodium, were examined and boron nitride was proved to have a different structure from graphite. Work has also been done on irradiation damage to crystal structure of these and simpler substances.

X-ray work has further dealt with the structure of compounds concerned with the trans-uranic and related fissile elements, such as the thorium halides, selenides and tellurides. Much work has been done on the properties of uranium and plutonium from the point of view of their metallurgical handling.

The important new contribution of Harwell to crystallographic studies has been the use of neutron diffraction which was started by G. E. Bacon and his co-workers in 1942. It is the only school of neutron crystallography in Britain. Bacon has concentrated on two kinds of problems for which neutron diffraction is especially suitable, the location of hydrogen atoms and the orientation of atomic magnets in compounds of transition elements. Starting with the ferro-electric KH_2PO_4, he was able to show that the hydrogen atoms in the hydrogen bond are not symmetrically placed and can be switched over to another oxygen atom by reversing the electric field. The bent nature of the hydrogen bond has, furthermore, been established in hydrated

salts and acids. The location of C—H bonds has been used to study thermal motions of molecules in crystals.

In the magnetic field, studies of spinels have been used to elucidate ferromagnetic and anti-ferromagnetic states where neutrons with their own magnetic moment can detect differences inaccessible to X-rays. A beginning has also been made in the study of inelastic scattering of neutrons where exchange of energy takes place between the neutrons and the acoustic and magnetic-spin waves in the crystal.

Building Research Station

The main work of the Building Research Station, which began with that of Dr. G. E. Bessey in 1930, was the study of structures of aluminates and silicates of interest to cement chemistry. This work has been continued by Drs. H. G. Midgley, E. Aruja and M. H. Roberts in close conjunction with work on similar silicates carried out at Birkbeck College (pg. 389). One complete structure, that of dicalcium silicate was worked out and the cell dimensions and characteristics of a large number of the silicates and aluminates have been determined, such as chlorites and serpentines.

The most interesting development has been the use of X-rays in the study of silicate and aluminate materials at high temperatures, and in the preparation of phase diagrams with F. M. Lea, T. W. Parker, R. Nurse and J. H. Welch. Most recently, a new form of high-temperature single-crystal X-ray camera was developed capable of giving X-ray pictures at up to 1800°C. Much work was also done on the development of quantitative determination of phase by X-ray methods.

Macaulay Institute for Soil Research, Aberdeen

This has been a pioneer in the study of clay minerals which have formed part of the survey of soils for Scotland. In 1939 Dr. D. M. C. MacEwan started there his series of studies on the identification of clay minerals by the absorption of glycerol ethylene glycol which is the basis of all modern clay analyses.

Dr. G. F. Walker has studied the structure of vermiculite and other soil constituents including the materials derived from the weathering of rock minerals. X-ray methods have been devised for separately assessing the quantities of the different clay minerals in a sample, and this is used in conjunction with other methods such as differential thermal analysis.

The Macaulay Institute has become one of the leading world centres of X-ray studies of clay minerals and has established X-rays as one of the major tools in pedological research.

Rothamsted Experimental Station, Harpenden

Pioneer work on X-ray studies of clay structures were initiated by G. Nagelschmidt in 1934. His work dealt with the structure, lattice shrinkage and structural formulas of the montmorillonite group of minerals, the clay mineralogy of soils and sediments, and methods of investigation of clay fractions. From 1945 to 1958, D. M. C. MacEwan continued the work he had started at the Macaulay Institute, Aberdeen, on the absorption and complex formation between organic molecules, particularly alcohols, and the minerals montmorillonite and halloysite. MacEwan in collaboration with G. Brown also worked on the interpretation of diffraction patterns from clays consisting of interstratified layers of different kinds. This work has been followed up by their co-worker R. Greene-Kelly and O. Talibudeen. G. Brown located the exchangeable cations in the glycerol-montmorillonite complex by one-dimensional Fourier syntheses. More recently he has applied single crystal X-ray methods to the study of weathering products. Here he has shown that a large number of soil mineral 'crystals' are actually topotactic mixtures of interstratified decomposition compounds.

Safety in Mines Research Establishment

The X-ray group, under the direction of Dr. Nagelschmidt, Dr. R. L. Gordon and now Dr. C. Casswell, has been mainly concerned with studies of the minerals in coal mine dust causing pneumoconiosis. This has led to the development of quantitative methods of analysis. A special study has been made of the disturbed surface layers on ground quartz.

The Medical Research Council

The Medical Research Council has for many years supported crystallographic research through its various External Research Units. The work of these units, however, was mainly concerned with macromolecules and in 1951 a small crystallographic laboratory was established at the National Institute for Medical Research, Mill Hill, London, under the direction of Mrs. O. Kennard. The laboratory has been engaged in research into Chemistry, Biochemistry and Biophysics and with applied research like Biological Standardization. X-ray diffraction methods have been adopted as routine techniques in these fields for identification, molecular weight determination and physical characterization in a variety of problems ranging from the identification of the thyroid hormone, triiodothyronine, after its first

isolation by R. Pitt-Rivers and J. Gross, to the diagnostic use of X-ray powder patterns in cystinosis. X-ray analytical work has been concentrated on organic compounds of moderate complexity, of which the structure of vitamin A acetate and the three-dimensional analysis of some steroidal sapogenins are examples, and to problems of bonding forces, as in the work on the structure of amidinium carboxylates. During the course of this work some new auxiliary techniques have been developed including a method of determining integrated intensities by the use of radioactive markers.

The laboratory has also been concerned with crystallographic documentation work and was responsible for the data on organic compounds in various compilations including the *Tables of Interatomic Distances in Molecules and Ions* and the projected second edition of *Crystal Data*.

17.5. CRYSTALLOGRAPHY IN BRITISH INDUSTRIAL LABORATORIES

by C. W. Bunn

The great harvest of knowledge of crystal structure resulting from the fundamental discoveries of von Laue and W. H. and W. L. Bragg began to flow freely in the decade 1920–30, chiefly from the Royal Institution under the guidance of W. H. Bragg, and Manchester University where W. L. Bragg was professor; and it was natural that under this stimulus crystallographic methods, especially X-ray diffraction methods, were soon taken up in industrial and government laboratories and used either for direct practical applications or for studying the crystal structures of materials used in various technologies. The simplest of the practical applications was the use of powder photographs for identification, for it was evident from the work of Debye and Scherrer that the X-ray diffraction pattern of a powdered crystalline material is an unrivalled 'fingerprint' of identity; it was soon used to settle many questions of identity which had not yielded to chemical methods or the older crystallographic methods (optical or morphological) owing to the opacity or submicroscopic size of the crystals. But in addition to this empirical application, more sophisticated methods such as the study of crystal orientation in metal sheets and wires, the estimation of crystal size and distortion from

broadened diffraction effects, and the study of atomic structure wherever it was felt that the knowledge was relevant, began to appear in non-academic laboratories.

One of the earliest organizations in the field was the General Electric Company, where F. S. Goucher at the Wembley Laboratories was studying the orientation of crystals in tungsten filaments by X-ray diffraction methods as early as 1923, and J. W. Ryde identified the crystals responsible for the scattering of light in certain opal glasses in 1926. H. P. Rooksby, who took part in some of this early work, has since then applied these methods to a great variety of problems. From 1930 onwards, with J. T. Randall, he made valuable contributions to our knowledge of the structure of glasses and liquids, and concluded that locally the atomic arrangement in these non-crystalline substances is similar to that found in crystals of the same substances. Other applications for which Rooksby was responsible, either alone or with others, range from the identification and quantitative analysis of refractory materials and thermionic cathode coatings to studies of the structures of ferromagnetic and antiferromagnetic crystals and luminescent materials, and metallurgical problems of lattice distortion and crystal orientation. This activity at the G.E.C. continues unabated.

In Imperial Chemical Industries, the first X-ray crystallography was done in the laboratories of Nobel Division at Stevenson in Ayrshire by F. D. Miles, who had worked for a time in Sir Wililam Bragg's group at the Royal Institution. Before 1930 he had followed the course of the nitration of cellulose fibres and studied the structure of cellulose trinitrate; later, he reported the crystallography of lead azide and other sensitive materials used as detonators. He also studied habit modification by dissolved impurities—a subject taken up again much later (1947–9) by J. Whetstone, with practical results in the control of the caking of ammonium nitrate. At Alkali Division at Northwich in Cheshire, C. W. Bunn, who had worked there on crystal growth problems and petrological methods of identification of inorganic substances since 1927, started using X-ray diffraction methods in 1933, first of all for identification but later for structure determination. Long-standing problems of inorganic chemistry which were cleared up by the use of X-ray powder photographs included the question of the constitution of the chlorinated lime product known as 'bleaching powder', the identity of the variously coloured precipitated iron oxide pigments, and the constitution of boiler scales, cements and plasters. The discovery of polythene there in 1933 led to an X-ray determination of its structure, and this started a series of similar investigations (with

E. V. Games and A. Turner-Jones) on other crystalline polymers such as rubber and related substances, and polyamides and polyesters. Meanwhile, other crystallographic work included further studies (with H. Emmett) of crystal growth from solution (the role of layer formation, surface structure and concentration gradients), the development (by H. S. Peiser) of the method of estimation of the degree of crystallinity in polymers which has since become one of the main technological applications of X-ray diffraction in the polymer field, contributions to methods of interpretation of X-ray diffraction patterns, and the determination of the crystal structure of sodium benzyl-penicillin (Bunn and Turner-Jones) which together with the work on the potassium and rubidium salts at Oxford (Hodgkin and Rogers-Low), settled the chemical constitution of that substance. The work on polymers was continued later (from 1946 on) at Plastics Division at Welwyn Garden City in Hertfordshire by Bunn, R. de P. Daubeny, D. R. Holmes and A. Turner-Jones; X-ray methods are used for characterizing new polymers, estimating crystallinity, studying crystal orientation in films and fibres, and for structure determination ('terylene', polyvinyl alcohol, nylon 6, polyisobutene, polytetra-fluoroethylene) as far as the pressure of practical affairs permits. Similar work is now done also at Fibres Division at Harrogate in Yorkshire, and at British Nylon Spinners at Pontypool.

During and after the war of 1939–45, X-ray crystallographic work was started in several other I.C.I. laboratories. At Metals Division in Birmingham, T.Ll. Richards studied crystal orientation in rolled metal sheets. At Dyestuffs Division in Manchester, A. F. Wells, who in earlier years solved several structures of inorganic and metal-organic compounds in various University laboratories, found time amidst the pressure of practical problems to develop a systematic treatment of network structures (those held together by localized directed bonds, as opposed to 'packing' structures where local directional effects are less important), while C. J. Brown and others concentrated on the structures of organic compounds much used in the Dyestuffs industry, such as aniline hydrochloride, p-aminophenol and acetanilide. At the Akers Laboratories at Welwyn in Hertfordshire, P. G. Owston and others, by solving several metal-organic structures, have played an important part in the development of the chemical studies of such substances by J. Chatt's group. At General Chemicals Division at Widnes in Lancashire, and Billingham Division at Stockton-on-Tees in Co. Durham, both X-ray diffraction and X-ray spectrographic methods are used for identification and quantitative analysis—as

indeed they are in many chemical laboratories in other organizations.

The development of the use of X-ray diffraction methods in the metallurgical, electrical and other industries in the North of England in the 'thirties owed a good deal to the encouragement of W. L. Bragg when he was Professor in Manchester, and to the existence of the group in his laboratory working on metallurgical problems under A. J. Bradley. A. H. Jay, who first worked on powder-camera design with Bradley, later applied powder methods to a variety of problems involving metals, alloys and refractory materials in the United Steel Companies laboratory at Stocksbridge. Others who made similar contributions were C. Sykes at Metropolitan-Vickers in Manchester, H. J. Goldschmidt at William Jessop and Sons Limited in Sheffield, and J. A. Darbyshire at Ferranti Limited in Manchester. Since that time the methods have been taken up in many laboratories, too numerous to mention individually. Most of this work is never published: it uses established methods and knowledge in order to fulfil its function in practical affairs, and makes a valuable contribution without necessarily revealing anything fundamentally new. Moreover, background studies of crystal structure can only be undertaken when the pressure of practical affairs is not too great; notable contributions of this sort were made by E. J. W. Whittaker (Ferodo Limited, Chapel-en-le-Frith, Cheshire) in his studies of the structure of chrysotile and the theory of diffraction by cylindrical lattices, and by V. Vand (Unilever Limited, Port Sunlight, Cheshire), who determined the structures of several organic chain compounds, discovered in a potassium soap a new type in which the chains are crossed, and contributed to the methods of interpretation of diffraction patterns.

Natural textile fibres like cotton, wool and silk, which were shown, very early in the history of X-ray diffraction, to contain oriented crystalline arrangements of molecules, offer good opportunities for both structure studies and technological applications. Much of the early work on the structures was done in academic laboratories—by Mark and Meyer and others on the continent and by Astbury in this country. X-ray methods were introduced at the Shirley Institute at Manchester in the early 'thirties by Dr. Pelton, who had worked under W. H. Bragg at the Royal Institution. They were at first used for technological problems, such as in the study of crystal orientation in cotton and its relation to the physical properties, but later on, more fundamental structural studies of cellulose and its derivatives and silk fibroin were undertaken by J. O. Warwicker and others. The British Rayon Research Association at Manchester also made contributions

in this field. In the laboratories of Courtauld's Limited, the group led by C. H. Bamford at Maidenhead, together with L. Brown at Coventry, have made very valuable contributions to our knowledge of the structure of the synthetic polypeptides, while C. Robinson discovered a very remarkable new type of liquid crystal structure in solutions of one of these substances.

The use of crystallographic methods in industry continues to grow. The extent and value of the work are not to be judged by the volume of published work, large though this is, for the majority of the work done is unpublished. Although a substantial amount of fundamental structure work has been done in industrial and government laboratories, and although new facts and phenomena are sometimes discovered and reported, the justification of the use of these methods in industry lies in the direct technological applications, such as identification and analysis, and the correlation of crystal size, orientation and texture with the properties of materials. Scientific discoveries and advances in fundamental understanding can and do come out of industrial research, but they are not usually regarded as primary objectives.

17.6. EARLY WORK AT UNIVERSITY COLLEGE, LONDON, 1915–1923

by Dame Kathleen Lonsdale

W. H. Bragg was appointed Quain Professor of Physics in 1915, but did not take up his duties fully until the end of World War I. Then he began to gather around him a group of young physicists which included:

I. Blackhurst, who studied thermal vibration effect on intensity, using the ionization spectrometer with diamond, graphite, aluminium and designed a Hg high-vacuum pump; and G. Shearer and A. Muller, who respectively developed home-made hot-wire and self-rectifying gas tubes for photographic studies of long-chain compounds. For this purpose they used foot-operated fore-vacuum pumps, home-made high-vacuum pumps and induction coils, and Wehnelt interrupters— constructed out of aluminium hot-water bottles.

W. T. Astbury joined the team in 1921 and used the ionization spectrometer, complete with Mo Coolidge tube (air-cooled), lead box, gold-leaf electroscope, Ruhmkorff coil with Hg interrupter, and

metronome (to time the rate at which the crystal was rotated through a reflecting position). He was fascinated by the problem of the optical activity of tartaric acid. His training in chemistry enabled him to understand better, probably, than any of the other workers the potentialities of the X-ray method of structure analysis in respect of the light it might throw on both physical and chemical problems of the solid state. His personality and enthusiasm led to the liveliest discussions in the laboratory and over joint meals, about everybody's research studies, crystallographic problems in general, politics, religion and almost everything under the sun.

Other workers in the UCL Physics department forty years ago included R. E. Gibbs (who studied the structure of quartz, with W.H.B.), W. G. Plummer (preliminary investigation of C_6Cl_6 and C_6Br_6, an isomorphous pair, by the photographic technique) and K. Yardley, who began the study of succinic acid and simultaneously the application of space-group theory to structure analysis. Thomas Lonsdale, to whom she was married five years later, also worked in the laboratory, but on the elastic properties of metal wires, under Professor Porter, whose main interests were in the phenomena of radiation and convection. (One of his more original lectures was entitled 'Why the Daddy-long-legs doesn't wear Stockings'!)

During this period W. H. Bragg himself worked mainly on the structures of anthracene, naphthalene and naphthalene derivatives. He noted that the difference in length of the c axis of anthracene and naphthalene, whose a, b axes and β angles were very similar, was about equal to the diameter of a six-membered carbon ring in the structure of diamond (which had been fully worked out) or in graphite (which had not, but the unit-cell dimensions and the fact that it was a layer-structure were known). From this he deduced the general dimensions and positions of the anthracene and naphthalene molecules, although he wrongly assumed the benzene nuclei to be 'puckered'; and the assumed orientation of the molecular normals in the (001) planes was not correct.

It is interesting, however, to note that he initiated the studies of *isostructural* series both of aromatic and of aliphatic compounds (long-chain paraffins, fatty acids, esters, alcohols, ketones, etc.) and was aware of the value of the *isomorphous* + *heavy atom* technique. Indeed in a paper on the structures of NaCl, KCl, KBr and KI (*Proc. Roy. Soc.* A*89*, 468, 1913) W. L. Bragg had written:

'By noticing what differences were caused in the photograph by the substitution of heavier for lighter atoms in the crystal, a definite

arrangement was decided on as that of the diffracting points of the crystalline grating.'

It was this that led to the examination of C_6Cl_6 and C_6Br_6 by W. G. Plummer and later to a study of the substituted ethanes by K. Yardley. Neither study was successful, however, at that time!

When W. H. Bragg moved to the Royal Institution in June 1923 he took most of this team with him, and for a time Professor Porter was head of the department. The Quain chair was held from 1928 onwards by E. N. da C. Andrade, whose main interest was in the mechanical properties of solids, especially metals, and in epitaxial growth, and who used X-ray techniques as an auxiliary tool.

17.7. CRYSTALLOGRAPHY AT THE ROYAL INSTITUTION

by Dame Kathleen Lonsdale

While Sir William Bragg was Quain Professor of Physics at University College, London, he gave a Friday Evening Royal Institution Discourse (19 May 1922) on 'The Structure of Organic Molecules'. In it he discussed naphthalene, anthracene, α- and β-naphthol and acenaphthene, all substances that he was then engaged in studying by means of X-ray diffraction, and he compared them with diamond and graphite, (although at that time it was not known that the graphite layers were plane) and showed that in all of them six-membered carbon rings were present. He had already invited to work with him at University College a group of young people, most of whom he took with him to the Royal Institution when, in June 1923, perhaps as the result of this lecture and of the course of Christmas lectures he gave in 1919, he went there to succeed Sir James Dewar as Director of the Davy-Faraday Laboratories and Fullerian Professor of Chemistry.

The Royal Institution, founded in 1799 by Benjamin Thompson, Count Rumford, had housed a succession of famous men such as Thomas Young, Humphrey Davy, Michael Faraday, John Tyndall and James Dewar, and the lectures delivered within its walls had covered almost every new discovery in science as well as a wide range of other subjects. Almost a century later (in 1896) the Davy-Faraday Laboratory, formerly a private house with many rooms, both large and small, had been added, by the munificence of Dr. Ludwig Mond, to

provide wider opportunities for research to men *and women* of any race or nationality. The historic laboratories in the Royal Institution had not been open to women; the early 19th century records plainly suggest that they would be expected to be only a nuisance there. On the other hand they had always been cordially invited to attend the Royal Institution Lectures; it would, as Thomas Young gracefully put it, be an alternative to their 'insipid consumption of superfluous time'. And their subscriptions were needed to maintain the Institution in the style to which it was accustomed.

W. H. Bragg included three women among the twelve research workers whom he had gathered around him by the autumn of 1923.* He found the Davy-Faraday Laboratory almost moribund. He made it not only into a lively international school of research but also into a centre to which famous men of science gravitated naturally when they were in London. As one of the Davy-Faraday research workers wrote to me recently: 'the triple appeal of laboratory, library and lectures was an inspiration. My main impressions were of the happy family atmosphere with formality in the background; the casual way world figures appeared at tea-break; the loose organization...; the dearth of mathematical texts marking the emphasis on experimental science.'

In spite of his mathematical background Sir William Bragg was indeed an experimentalist. He did encourage his students to study mathematical crystallography, but it was in order to apply it, not as an end in itself. He was keenly interested in the discussions that went on in the laboratory concerning the extent to which the molecular symmetry was used in the building of crystal symmetry. The results of these discussions had been partly summarized in what were called 'Shearer's Rules', which expressed the empirical fact that up to that time no structure had been found in which the 'asymmetric unit' contained more than one molecule, although it was sometimes a sub-multiple of the molecule. Sir William was not so keen on the idea of tabulating all the symmetry properties of the 230 space groups and their implications in terms of diffraction theory. He felt that this savoured of mathematical perfectionism and that it was simpler and more realistic to examine each case as it occurred in the course of research. (In later days he never became wholly reconciled to the use of reciprocal space; and preferred a more complicated but, as he felt, more realistic picture of what was actually happening to the X-ray

---

* W. T. Astbury, J. D. Bernal, R. E. Gibbs, L. C. Jackson, Miss I. E. Knaggs, Miss G. Mocatta, A. Muller, W. G. Plummer, G. Shearer, C. H. Weiss, J. F. Wood and Miss K. Yardley. In all, 12 of the 70 workers admitted before 1940 were women.

beam within the crystal.) But he allowed himself to be convinced that the Astbury-Yardley Tables were worth publishing and then he convinced the Royal Society that they were worth the considerable expense involved in having the 230 diagrams professionally re-drawn for publication. It was one of the few *Philosophical Transactions* publications that had to be reprinted.

Those of us who worked with W. H. Bragg in the Davy-Faraday Laboratory got the impression that we were allowed to choose and develop our own research themes entirely independently. Sir William certainly never dictated; and he expected his team (later classified in the D.F. records as 'Research Assistants' who were in receipt of an annually renewed salary and 'Research Workers' who were of independent means or in receipt of supporting grants) to have original ideas and to develop them independently. But, looking back, it is possible to see that in fact he directed the research by means of silken reins that were hardly felt but were very effective.

To begin with, it was understood that we would choose some problem connected with organic structures. Apart perhaps from quartz, which had interested Sir William since 1914, the inorganic world was left to the Manchester school under his son, W. L. Bragg. Then he guided the general trend of research by injecting, from time to time, a new worker having a different background and outlook. Miss Knaggs, for example, had worked with Professors Pope and Hutchinson at Cambridge and brought with her the ideas of the importance of valency and spatial considerations in determining structures and a wide knowledge of mineralogical and optical methods. J. M. Robertson was first and foremost a chemist, whereas the earlier workers all had a background of training in physics; Miss Woodward was a mathematician; and A. R. Ubbelohde, who has described himself as the Benjamin of the family, was interested primarily in the thermodynamical problems of crystals. But the principal way in which Sir William guided us without our really being aware of it was by asking us to help him with the preparation of lectures. He had a habit of taking subjects of research in the D. F. Laboratory, thinking about them, looking up related papers, talking about them to visitors and then lecturing about them so clearly that the research worker engaged on the problem became aware of all sorts of possibilities that he had somehow overlooked before. Early in 1926 Sir William gave an afternoon course of R.I. lectures on 'The Imperfect Crystallization of Common Things', which was repeated with additions in the autumn. He asked W. T. Astbury to assist him in the preparation of this lecture

by taking X-ray photographs of natural fibres, such as were being taken at the Kaiser-Wilhelm-Institut für Faserstoffchemie. This Astbury did with such thoroughness that he became interested in the field and when an opening occurred in Leeds for an X-ray physicist to study textile fibres, W. H. Bragg persuaded Astbury to go. He needed a good deal of persuasion; none of the workers in the D.F. Laboratory ever wanted to go. The salaries there were not particularly good, but the atmosphere was so pleasant that the idea of staying on indefinitely was most alluring. But if Sir William thought that one of his people was ready to take more responsibility and if a suitable job presented itself, he pretty well pushed them out.

It really was astonishing that he should have had such vigour, for although we affectionately called him 'the old man' none of us really thought of him as old. He was still publishing vigorously when in his 80th year, and seemed to have the mind of a young man, able to take a keen interest in such a new phenomenon as the diffuse scattering of X-rays due to thermal vibrations.

When I look back at the early days at the Davy-Faraday Laboratory disconnected memories come to the surface. We had plenty of time for discussion. It was not possible to sit *all* day long with one eye glued to a microscope taking readings of the movements of a gold leaf, although quite a lot of our time was spent this way. From time to time our Hg interrupters had to be thoroughly cleaned out, a filthy job; but we could do it and talk simultaneously. Several of us brought sandwiches and lunched together in a room on the premises and then played table tennis in the basement afterwards. Within a year or two we could put on international tournaments: France was represented by C. H. Weiss (study of alloys) and later by M. Mathieu and M. J. H. Ponte (scattering factor of the carbon atom); Holland by W. G. Burgers (study of i-erythritol and other crystals too complicated to solve then); the Soviet Union by Boris Orelkin (preliminary study of 1,3,5-triphenyl-benzene). W. T. Astbury (who was universally known as 'Bill' and who insisted on calling everyone else—including me—'Bill' also) was the life and soul of these table tennis sessions and introduced various hazards, such as matchboxes at strategic points on the table, to make them more exciting. Most of us were pretty good.

Tea-time at 4 p.m. was something not to be missed. To begin with, W. H. Bragg was nearly always there and there were generally Bourbon biscuits too. And all sorts of interesting visitors turned up. Some of them were Friday Evening lecturers come to prepare the experiments for their discourses. It might be Sir Ernest (afterwards

Lord) Rutherford, about to talk on the 'Life History of an α-particle from Radium' or on the 'Nucleus of the Atom'; J. H. Jeans on 'The Origin of the Solar System'; H. E. Armstrong on the 'Scientific work of Sir James Dewar'; G. Elliott Smith on the 'Human Brain' or Lord Rayleigh on the 'Glow of Phosphorus' or Charles Darwin on 'Recent Developments in Magnetism'; Sir William Pope on 'Faraday as a Chemist' or Sir J. J. Thomson on 'Radiation from Electric Discharges'. Or sometimes there were rich business men from whom Sir William was busy extracting money for the D.F. Laboratory. One I particularly remember was one of Sir William's own past students who was quite disturbed that Sir William's talents were being wasted in such a dead-end, poorly-rewarded job when he might be making top money, as he himself had done.

From time to time there were open days, or 'conversaziones', at the Royal Institution (as there still are), and these involved the con-struction of illustrative charts and models which we had to be prepared to discuss with experts and laymen alike. (One old lady asked Sir William why his naphthalene model didn't smell like mothballs?) Or Sir William would himself bring an eminent visitor round the labora-tory. One visit that has remained in my memory was that of Sir Alfred Yarrow, who had endowed some attractive research fellowships. He propounded a theory that brilliant men inherited their intellect on the *maternal* side and asked Sir William what he knew about his mother's people? Sir William, looking slightly embarrassed, said all he knew was that they had something to do with the Church. Sir Alfred went on, rather inconsistently, to deplore the fact that young women scientists were apt to leave their professions in order to get married and was taken aback when I asked where his intelligent mothers would come from if only those with no professions were allowed to marry?

The Royal Institution library was well-stocked with books (although not on the mathematical side, as has already been remarked) and especially with periodicals. It was thrilling occasionally to open a very early back number of, say, the *Phil. Trans. Roy. Soc.*, and find that Faraday had made some comment in the margin, and even more thrilling to meet an aged member of the R.I. (Mr. William Stone) who remembered, as a small boy, sitting next to Faraday and talking to him, in the gallery of the R.I. Lecture Theatre, during some Christmas Lectures. Much of the early historical apparatus, both research and demonstration, was also kept in the Royal Institution, and occasionally one could find, in bottles that had not been disturbed

for many years, simply enormous single crystals that had grown very very slowly by sublimation on to the walls. When work was begun on the magnetic anisotropy of crystals these were exceedingly useiul, because the use of large crystals minimized the effect of the suspension.

It would be impossible to mention apparatus and crystals without speaking of Mr. Jenkinson and Mr. Smith. Mr. Jenkinson we called 'Jenk' in our irreverent moments when he was not there but never when he was, whereas 'Smithy' was so-called to his face and liked it. Mr. Jenkinson had come from University College with Sir William and was a superb instrument maker. He made the ionization spectrometers and gold-leaf electroscopes (but we put on our own gold leaf if we could, although he would show us how to, the first time). He made the ionization chambers (but we filled them) and had an assistant (who for many years now has been head of his own crystallographic instrument workshop) who helped to make the huge lead-covered box that housed both the Coolidge tube and the electric fan used to cool it. What exotic radiations we used: Mo, Rh, Pd, as a rule! Even with the fan, the anticathode would get white-hot after a short time of running. Our one fear was lest we should become so mesmerized with taking readings of the movements of the gold-leaf to the sound of the metronome by our side that we would forget to look down the collimator to see the colour of the massive target before it *sagged*. While the tube cooled off, we recorded our measurements and interpreted them. We ran the Coolidge tube with an induction coil and the aforesaid Hg interrupter, with a condenser in parallel. In the *secondary* circuit there were a milliameter and a spark-gap. The latter was set so that we got both a visible and an audible signal if the voltage rose above the 60 KV which was the normal running condition. These stood, with a battery of accumulators that gave us the voltage for our ionization chamber, on a small insulated table just at the side of the lead box. By stretching out our hand we could just touch it. We had to remember *not* to. I am not the only worker whose hair has stood permanently on end, more or less, ever since.

Smithy was the laboratory steward, but he was much more than that. He was skilful with his hands and could make the pyrex high-vacuum pumps, originally designed by I. Backhurst at University College, better than anyone else. If we could not find the leaks in the gas tubes used for photographic work (that gradually replaced the ionization method), Smithy would help us. Later he took entire charge of the maintenance and running of the 5 kW tube and could design all kinds of auxiliary equipment for special purposes; and when Drs. Müller and

Clay were both absent through illness he ran and repaired the 50 kW equipment also. The 2 metre diameter spectrometer and 50 kW tube used in combination gave really good resolution, but the outfit was not foolproof enough to become standard equipment.

Mr. Green, the lecture assistant in the Royal Institution, was also very helpful with ideas if asked, but although workers in the D.F. Laboratory were permitted, by grace, to use the R.I. library, they were not expected to make themselves too free of R.I. facilities unless they became Members of the Royal Institution, which not all of them could afford to do. It paid off very well if one could, but in those days the 5 guinea entrance fee and 5 guinea annual subscription seemed a terrible lot of money. Sir William was sometimes called in to soothe old gentlemen snoozing in the upper library who complained that the young D.F. workers had disturbed them by *walking through*. He was excellent at soothing. I doubt, however, whether even he could have soothed the indignant passer-by who brought in from Albemarle Street the pieces of a steel file that had been hurled out of a third-floor window by the irritable worker in whose hands it had broken.

Mention has been made of the international character of the Davy-Faraday research school. Apart from those already mentioned, there were Miss N.C.B. Allen (Australia), A. L. Patterson (Canada), C. C. Murdock (U.S.A.), M. Prasad (India), W. H. Barnes (Canada), W. P. Jesse (U.S.A.), Miss T. C. Marwick (New Zealand), D. O. Sproule (Canada), Miss B. Karlik (Austria), A. A. Lebedeff (U.S.S.R.), F. Halle (Germany), N. Japolsky (U.S.S.R.), K. Banerjee (India), Miss L. W. Pickett (U.S.A.) and E. Pohland (Germany), who had come, in that order, before the end of 1932.

In 1933–5 several refugee scientists from Nazi Germany found a welcome in the D. F. laboratories: R. Eisenschitz, G. Nagelschmidt, A. Schallamach, A. Lowenbein. Then in 1938–9 came W. Boas (Germany and Australia), J. J. de Lange (Holland), L. O. Brockway (U.S.A.) and J. Monvoisin (France).

Most of these have since become heads of departments or of institutions, in various parts of the world.

The same is true, of course, of the British workers, although by now some of them have retired or died. Five * of the twenty-four pre-1930 vintage have become Fellows of the Royal Society, and all these established flourishing crystallographic schools in Universities. Others went into Government service or industry; or obtained senior academic

---

* W. T. Astbury, J. D. Bernal, E. G. Cox, K. Yardley (Mrs. Lonsdale), J. M. Robertson.

posts. The second or even third generation of crystallographers are now making their own marks on the pages of scientific history.

W. H. Bragg did not regard it as any part of his duty to *train* or *teach* research workers. The Ph. D. student who expected to be spoon-fed with pre-digested pap would have had short shrift from him. Unless a worker had some interesting results to show him, or some promising problem to discuss, he simply took no notice of him and in due course he disappeared quietly from the scene. He treated all his people as responsible colleagues and gave them the encouragement they needed; he found money and facilities for them. But he expected them to build their own apparatus out of bits and pieces, or to superintend its making in the workshops;—and above all he did not expect, except in the indirect ways mentioned earlier, to produce research problems for them or to have to tell them what to do next. He did insist on seeing the manuscripts of papers before they were sent for publication, and if he thought them worthy of it, he would communicate them to the Royal Society. An almost complete record of the research work done can be found in the *Proc. Roy. Soc.* and the *J. Chem. Soc.* (London) or for the later R.I. period (from 1937) in the *Research Abstracts* in the *Proc. Roy. Institution.*

It is only possible to give some of the highlights here. Early attempts on the crystal structure analysis of aliphatic and aromatic compounds were largely unsuccessful, apart from those of the series of long-chain compounds. These were prepared by W. B. Saville (1923–34), J. W. H. Oldham (1936–) and later by Miss H. Gilchrist (1927–37); and studied by A. Müller and G. Shearer. Shearer's greatest triumph was in the correct identification, by X-ray measurements of spacing and intensity only, of the values of n and m, first in a single long-chain ketone $CH_3(CH_2)_nCO(CH_2)_mCH_3$, and then in a mixture of two such ketones. These were prepared for him by Professor (later Sir) Robert Robertson, who as a chemist was greatly impressed by this proof of the power of the new method. Müller, who later became Assistant Director, designed a successful 'Spinning Target X-ray Generator' (water-cooled) as early as 1929. He was particularly interested, not merely in the structures of the odd- and even-numbered chain compounds and of the 'state of rotation' that set in a little below the melting point for some of them, but in their related physical properties (lattice energy, dielectric polarization, torsional flexibility, etc.).

W. H. Bragg had long been puzzled (as Faraday was before him) by the hardening of metals produced by cold-working. In February 1924 he gave an R.I. Discourse on the research work going on in the

D.F. Laboratory in which he referred to X-ray studies by Müller of Au, Ag, Cu and Al leaf or foil. Some work on metal structure continued in a minor way until 1951, when under Professor Andrade it became a major interest in the laboratory.

In 1924 J. D. Bernal (independently of Hassel and Mark) successfully proved the planarity of the layers in graphite, but his crowning achievements were the production of charts for the interpretation of X-ray single-crystal rotation photographs and the design of a universal X-ray photogoniometer. W. T. Astbury, in addition to attempting the structure analyses of tartaric acid and of Al and Ga acetylacetones, produced an ingenious integrating photometer for the photographic method. E. G. Cox and W. F. B. Shaw worked out correction factors for photographic measurement of intensities, and Cox also made the earliest determination of the structure of benzene. W. H. Barnes studied the structure of ice from 0°C to −183°C. Later Mrs. Lonsdale was able to take 'Laue' photographs of the diffuse scattering from ice grown on the D.F. Laboratory roof, simply by opening the windows of the laboratory on a wintry day and thus making the whole room into a refrigerator. It was not possible, however, to give an exposure of longer than about half an hour, because by then the X-ray beam had bored a neat hole right through the ice plate. Hailstones collected from the windowsill were also studied.

J. M. Robertson, who spent altogether some twelve years in the D.F. Laboratory, carried out a series of brilliant investigations of the crystal structures of aromatic compounds, beginning with naphthalene, anthracene, resorcinol, durene and benzophenone; and going on, partly with the later collaboration of Ida Woodward, to oxalic acid dihydrate, the phthalocyanines and the dibenzyl series, including stilbene, tolane, trans- and cis-azobenzene. He was particularly interested in the development both of special apparatus and numerical and mechanical computing techniques; and made great advances in the use of isomorphous and isostructural series and of the heavy-atom methods. Together with A. R. Ubbelohde he studied the effects of isotopic replacement (H by D) and of transitions such as $\alpha \rightarrow \beta$ resorcinol, and he carried out most valuable work on the relationship between bond character and interatomic distance, on the basis of his Fourier analyses.

A. R. Ubbelohde, in addition to his work in collaboration with J. M. Robertson, made fundamental investigations on the thermodynamic properties of the metallic state, on the mechanisms of combustion of hydrocarbons, on melting and on various irreversible processes.

Sir William's interest in fibre structure has already been mentioned. In 1933 he extended this to include 'crystals of the living body' and in a lecture which included references to the work of W. T. Astbury (Leeds) on silk, wool, nerve and muscle, and to that of J. D. Bernal (Cambridge) on the aminoacids, vitamins etc., he emphasized especially that it was now becoming possible to correlate the magnetic, electric, optical and thermal properties of crystals with their structure and, conversely, to use such properties to assist in the determination of unknown structures.

From 1932 onwards measurements of the diamagnetic anisotropy of aromatic and aliphatic crystals were made first by Mrs. M. E. Boyland, then by Mrs. K. Lonsdale with assistance from C. H. Carlisle and in parallel with structure determinations. Some horrible risks were taken in ignorance. For example, Miss Knaggs published a structure of cyanuric triazide, for which magnetic measurements were made by Mrs. Lonsdale. Professor K. S. Krishnan, then in Calcutta, decided to repeat some of these measurements; but the crystals, which are a somewhat erratic explosive, detonated overnight and wrecked his laboratory. The D.F. Laboratory evidently had a better guardian angel.

In 1933 W. H. Bragg became absorbed in the problem of so-called 'liquid crystals', following a general discussion at the Faraday Society in April of that year. The lecture in which he gave an account of the optical effects shown by smectic, nematic and cholesteric classes was one of the few in which he showed that his fundamental mathematical training could still stand him in good stead. His later interest in clays derived partly from the Christmas lectures he had given on 'Old Trades and New Knowledge', partly from his son's work on the silicates and partly from the current investigations being made in the D.F. Laboratory by G. Nagelschmidt.

Shortly before Sir William's death in 1942 there began in the laboratories and elsewhere the studies of diffuse scattering by the thermal waves in crystals and of the anomalous scattering in type I diamonds which interested him so much that he arranged a Royal Society Discussion on the subject. These researches were continued during the subsequent years when first Sir Henry Dale and then Professor E. Rideal was Director of the D.F. Laboratory. At the same time Miss Woodward and A. R. Ubbelohde were studying the sub-crystalline changes in structure of Rochelle salt and potassium dihydrogen phosphate in their ferroelectric regions, and studies of texture and extinction were being made by means of Laue and divergent-beam photographs. In 1950 L. R. G. Treloar began his

studies of polymers and D. P. Riley those of DNA and other globular proteins, while the coming of Professor Andrade as Director in 1951 brought R. King to study metals and U. W. Arndt to develop Geiger and proportional counters for intensity measurements.

Since 1954, when Sir Lawrence came from the Cavendish Laboratory to take the position formerly held by his father, the laboratories have developed very much along these three lines: the study of metal structures (illustrated by the delightful Nye-Bragg bubble models); the building of equipment for the automatic recording of large quantities of crystal data; and with the help of A. C. T. North, D. W. Green, D. C. Phillips and Miss Helen Scouloudi, and in collaboration with the Cambridge Medical Research Council Unit, the successful attack on the sperm whale and seal myoglobin structures.

Less than 40 years from naphthalene and anthracene to the structures of complicated protein crystals: what a pity that Sir William did not live to see the latter! One feels that even at 100 years old he would still have been thrilled at this crowning achievement of the science that he helped to found.

17.8. EARLY WORK ON CRYSTAL STRUCTURE AT MANCHESTER

by R. W. James

Manchester's connection with the diffraction of X-rays by crystals began very shortly after the discovery of the effect at Munich, when H. G. J. Moseley, working in Rutherford's laboratory, and following up W. H. Bragg's discovery that the characteristic X-ray spectra from the elements were line spectra, used a crystal as an optical grating to establish his famous relation between the characteristic frequencies and the atomic numbers of the elements. At the same time, C. G. Darwin, then Lecturer in Mathematical Physics in the laboratory, extended W. L. Bragg's treatment of diffraction by crystals, taking into account multiple reflections from plane to plane within the crystal, which Bragg had neglected. He showed that a crystal with small absorption, consisting of a perfectly ordered array of planes, should reflect the radiation totally over a very small range of angles, proportional to the amplitude scattered by a single crystal unit, and that the middle of this range occurred at an angle rather greater than that given by the

simple Bragg law. He showed too that while total reflection was taking place the rays could penetrate only to a very small depth in the crystal, an effect known as primary extinction; and he obtained an expression for the refractive index of the crystal for X-rays *less* than unity by a few parts in one hundred thousand.

On Darwin's theory the integrated intensity as the angle of incidence varied through the reflecting range ought to be proportional to the first power of the amplitude scattered by a single crystal unit, but if multiple reflections were neglected it should be proportional to the square of this quantity. Moseley and Darwin made some measurements with rocksalt and white radiation to try to test this point, and found results that seemed rather to support the simpler theory. This work was published in 1913 and 1914 in two remarkable papers that laid the foundations of the quantitative measurement of the intensities of X-ray spectra, and drew attention at the very outset to what has always been the main difficulty in such work, allowance for the state of perfection of the crystal. Because of the war, the implications of Darwin's work were not at once appreciated, and meanwhile Ewald had handled the same problem in a more fundamental manner in his dynamical theory; but his papers too were overshadowed by the war, and did not become well known in England until some years after their publication.

In 1919 W. L. Bragg succeeded Rutherford in the Manchester chair, and one of his first objects was to put reflection of X-rays by crystals on a proper quantitative basis. With this end in view he, with R. W. James and C. H. Bosanquet, began a series of measurements of the absolute intensity of reflection of X-rays from rocksalt, a crystal whose structure was definitely known, with no uncertain parameters. In this way it was hoped to test the applicability of the reflection formulas. It was realized, moreover, that in view of the relation of the wavelength of the radiation to the dimensions of the atoms the amplitude scattered by an atom would not be proportional at all angles to the number of electrons it contained, but would decrease with increasing angle of scattering, merely as a consequence of the increasing phase differences between the contributions scattered by the different parts of the atom. The measurement of the so-called f-factor, the ratio of the amplitude scattered by an atom to that scattered by a single classical electron under the same conditions, was one of the aims of these experiments; for, in the first place, from its angular variations it was hoped to get direct optical evidence of the distribution of the electrons in the atoms, and secondly, it was clear that information about the way

in which the scattering powers of different atoms depended on the angle of scattering would be essential if any but the simplest crystals were to be analysed.

The apparatus available for this work was by modern standards primitive. An ionization spectrometer was used, one of the original instruments constructed in W. H. Bragg's laboratory at Leeds, which was to have another good fifteen years of useful life at Manchester. The source of radiation was at first a gas tube, excited by an induction coil with a Wehnelt interrupter; and conditions were often so unsteady that it was impossible to obtain readings of any real value. A little later, when the gas tube was replaced by a Coolidge tube, and the induction coil by a more suitable transformer, reproducible results of fair accuracy were obtained. The integrated reflection was measured by a method first suggested by W. H. Bragg, in which the crystal was rotated through the reflecting range with a uniform angular velocity, the total ionization produced in the chamber during the rotation being taken as a measure of the intensity. The lead-screw of the crystal table was fitted with a capstan-head with four spokes, and this was turned by the index finger of the observer, one flick of the capstan to each beat of a metronome, a simple device that proved surprisingly adequate. For absolute measurements the radiation had to be made mono-chromatic by reflection from a crystal, for which purpose resorcinol was used in these experiments, and then reflected a second time from the rocksalt crystal. After two reflections the intensity was small, and only strong spectra could be measured in this way.

The rocksalt crystals used in these experiments were found to reflect very nearly according to the simple formula that neglected multiple scattering, and the more intense spectra were as much as twenty or thirty times stronger than the Darwin perfect-crystal formula indicated. It was noticed, however, that these strong intensities varied consider-ably from specimen to specimen. A freshly cleaved face might give an abnormally low reflection, but this could perhaps be increased eight or ten-fold by grinding the face on fairly coarse emery paper, and it was found too that as a result of this treatment the intensities from different specimens tended to approach the same limit.

It appeared that, if crystals were so imperfect that exact regularity did not persist over a large enough region for the Ewald-Darwin dynamical field to be set up within it, the formula that neglected multiple reflection still applied. Ewald suggested the name *mosaic* for crystals of this kind, and the experiments suggested that the Manchester rocksalt crystals approached this type closely. But even so, the strong

spectra were weaker than they should have been, and this was ascribed to the shielding of regions deeper in the crystals by nearly parallel regions above them, which reflected away radiation that would otherwise have reached them. This shielding effect was reduced by grinding, which presumably reduced the degree of parallelism of the different regions, but it could not be entirely removed. Darwin called this effect *secondary extinction*, although it is of course of quite a different nature from primary extinction in perfect crystals. It proved possible to estimate the enhanced linear absorption due to this effect, and to some extent to correct for it; and ultimately a set of absolute f-curves for sodium and chlorine were obtained which were in fair agreement with what was to be expected from what was known at the time of the electron distribution in these atoms. Bragg, James and Bosanquet published these results in three papers that appeared in 1921 and 1922, and their implication in terms of crystal perfection was discussed by Darwin soon afterwards.

The choice of the very imperfect crystal rocksalt for these experiments was fortunate, for it led to fairly unambiguous results; but it was soon clear that not all crystals behaved in the same way. W. H. Bragg, for example, observed the reflections from a diamond to be nearly proportional to the structure factors, and not to their square as the mosaic theory required. There was considerable lack of understanding among many practical workers of the implications of the dynamical theory, which was not easy to read; and there was a corresponding ignorance on the part of the theorists as to how much crystals did actually reflect, as distinct from what, on certain assumptions as to their nature, they ought to reflect. Ewald, who had kept in touch with the work at Manchester and elsewhere, realizing this, organized in September 1925 an informal conference at Holzhausen in Bavaria, consisting of about a dozen members, and in a week's discussion a great advance in the general understanding of this rather difficult subject was made. It became clear that the perfect crystal is rather rare, that most crystals are neither perfect nor mosaic, but something between the two, and that the most reliable test of perfection or imperfection is probably the intensity with which they reflect X-rays. The problem, if not solved, had become defined. It seems proper to mention this conference in discussing the Manchester work, for the Manchester measurements had a good deal to do with its being held, and the Holzhausen discussion certainly had a great influence on later work there. It may be interesting to mention the members of the conference. They were P. P. Ewald, M. von Laue, W. L. Bragg,

P. Debye, C. G. Darwin, L. Brillouin, H. Mark, K. Herzfeld, I. Waller, H. Ott, A. D. Fokker, R. W. G. Wyckoff and R. W. James.

In 1925, D. R. Hartree, afterwards Professor of Applied Mathematics at Manchester, but then still at Cambridge, calculated average electron distributions for sodium and chlorine atoms based on the Bohr orbit model of the atom. The *f*-curves calculated from these distributions fell away less uniformly and less rapidly than the measured curves, and the effect was one not to be explained by an imperfect knowledge of the temperature factor. It was in fact mainly due to the concentration of charge density at certain radii produced by averaging the circular orbits of the Bohr model.

In the same paper Hartree estimated the dimensions of the atomic orbits for a number of ions, and *f*-curves based on these were used by James and W. A. Wood in a determination of the structure of barytes, published in 1925. There is little doubt that the obvious need of crystallographers for reliable information about *f*-factors had considerable effect in directing Hartree's attention to the calculation of atomic electron distributions, and so led him to devise the method of the self-consistent field.

The effect of the thermal vibrations of the atoms in reducing the intensities of X-ray spectra had been pointed out by Debye, and demonstrated experimentally in 1914 by W. H. Bragg. James continued the experimental work on rocksalt by measuring the intensities of a number of spectra from room temperature to 600°C in 1925, and in 1926 and 1927, with Miss E. M. Firth (Mrs. W. Taylor), extended the measurements to the temperature of liquid air. By this time Schrödinger's theory had been developed, and Hartree had calculated the atomic wave-functions of sodium and chlorine by the method of the self-consistent field. Wentzel had shown that for the usual X-ray wave-lengths the scattering of radiation from an atom could be obtained by treating the Schrödinger charge distribution as a classical charge distribution, and Waller had extended Debye's theory of the temperature effect. A detailed comparison with theory was therefore possible. In papers published in 1927, which had their origin in a visit to Manchester of Ivar Waller of Uppsala, he with Hartree and James showed that there was good absolute agreement between the measured and calculated *f*-curves, provided that in allowing for the temperature correction the existence of zero-point energy was assumed; and these results were confirmed by James, Brindley and Wood with potassium chloride, and with aluminium.

Concurrently with the quantitative work a considerable amount of

structure determination had been going on in the laboratory, and in due course two main lines of investigation developed, those on the structure of the silicates and the structure of the alloys. Bragg insisted that structure determination ought to be considered primarily as a physical problem, and not merely as a geometrical one, and that, to make progress, relevant information of all kinds should be sought and used. A structure determination was in those days usually a matter of trial and error, and success was likely to depend on the skill and physical insight displayed in guessing an initial structure. That Bragg himself possessed this particular skill in an unusual degree was a great factor for success in the work. Ideas of what was a suitable crystal for a structure determination were still largely governed by whether it could be obtained in specimens large enough for use on the spectrometer, and whether it had a high symmetry. It was customary to grind faces on the crystals if they did not occur naturally. Another technique in which a slice of crystal was mounted on the spectrometer in such a way that it could be rotated in its own plane was often used, and in this way, by reflecting through the slice from planes perpendicular to its surface, the intensities of spectra round a zone axis could be compared with considerable accuracy. Photographic methods came into use comparatively slowly, and were mostly limited to oscillation photographs, first with flat photographic plates, and afterwards with cylindrical cameras.

Bragg laid stress on the idea that an atom in a crystal had a characteristic size, and that in deciding on likely structures packing had to be taken into account. He encouraged his pupils to make models, and to see how best the available material would fit into the available space. A structure ought to look sensible, to be so to speak a good engineering job. In 1920 he showed that in many crystals interatomic distances obeyed a simple additive law, and these results were reinterpreted in 1923 by Wasastjerna in terms of atomic sizes, and checked by atomic refractivities. To the same period belong papers by Bragg on the refractive indices of calcite and aragonite, in which the double refraction is calculated by taking into account the varying interaction in different directions of the atomic dipoles produced by the optical electric fields.

The realization that the refractivity in such compounds was due principally to the relatively large and easily polarizable oxygen atoms was of influence in the early development of the work on silicates; for it was seen that many of the simpler silicates could be regarded very nearly as an array of close-packed oxygen atoms, with the relatively

small metallic ions tucked in the crannies between them, the crystal as a whole having a refractive index not very different from that of a close-packed array of oxygen. Bragg saw that the ruby, Al_2O_3, not of course a silicate, could be regarded in this way, and the same idea was of importance in some of the earlier silicate analyses. An interesting example was cyanite, which although triclinic, was seen to be essentially, so far as packing was concerned, a close-packed array of oxygen.

From 1926 onwards a long series of papers by Bragg himself, by his own Manchester pupils, and by many workers from laboratories abroad, issued from the laboratory. It was found that the silicon atoms always lay at the centres of tetrahedra formed by four oxygen atoms. In the orthosilicates these were independent groups, but sometimes by sharing oxygen atoms they might form rings, or endless chains, or ribbons in which two parallel chains shared oxygen atoms, as in the fibrous minerals like asbestos; or they might form sheets of linked hexagonal rings, as in the flaky minerals like mica or talc; or they might form cage-like structures in three dimensions, as in the felspars and zeolites. These extended groups are in effect extended negative ions, and valency requirements must be fulfilled when they build into a structure by including suitable positive ions. The extreme variability in composition of the silicates is accounted for by the fact that in these groups a certain number of silicon atoms may be replaced by aluminium, which alters the effective valency of the group, and allows a corresponding variation in the number and nature of the metallic ions in the structure. Bragg showed as a result of this work that the chemistry of the silicates was a chemistry of the solid state, intelligible only in terms of the three-dimensional structures. Quite precise valency requirements have none the less to be obeyed, and this was well understood and used by the Manchester workers sometime before the full development of the idea by Pauling.

These structures were at the time among the most complex that had been attempted, and a paper by W. L. Bragg and J. West, who took a large share in the silicate analyses and in the training of those who worked on it, entitled 'A Technique for the X-ray Examination of Structures with Many Parameters', was published in the *Zeitschrift für Kristallographie* in 1928, and summarized the methods then in use in the laboratory.

A very important development in 1929 was the introduction by Bragg of the method of two-dimensional Fourier synthesis, which was first applied, as an illustration, to the analysis of one of the silicates,

diopside, the structure of which had been obtained by other methods. The importance of the method was that it allowed all available measurements to be used in the determination of the structure, and it rapidly became and has remained, a standard method of crystal analysis. The work on silicates lasted from ten to twelve years at Manchester. A very active worker was W. H. Taylor, now Head of the Crystallography Department of the Cavendish Laboratory, who made the silicates and zeolites his special field and has continued to work on them.

The use of powdered-crystal methods in the laboratory was developed by A. J. Bradley and J. C. M. Brentano. The latter was interested in its development as a method of obtaining quantitative measurements of intensities, unaffected by secondary extinction. Bradley was responsible for developing the Debye-Scherrer method and for applying it to a long series of determinations of alloy structures. He began work with a small and rather primitive powder camera and a Shearer gas tube, and with this he determined the structure of the hexagonal crystal lithium potassium sulphate, making perhaps the first attempt to allow for the decrease of scattering power of oxygen with increasing angle of scattering. The structures of arsenic, selenium and tellurium followed in 1925, and this led on to work on the structure of alloys that occupied Bradley and his fellow workers for the next twelve or fourteen years. He greatly improved the powder technique, and with A. H. Jay in 1932, made it into a precision method for the determination of lattice spacings. The work on alloys was helped by Messrs. Metropolitan Vickers of Trafford Park, who installed a vacuum induction furnace for the preparation of the alloys, and a number of members of their research department, among them Dr. C. Sykes, worked from time to time in the laboratory.

Notable achievements were the determination of the structure of γ-brass, with 52 atoms to the unit cell, and the recognition of the relation of the γ-phase to the simpler β-phase in such alloys; and of the structure of α-manganese, with 58 atoms to the unit cell, by Bradley and Thewlis. These, and the later determinations of the structures of phosphotungstic acid by Bradley and Keggin, and of phosphomolybdic acid by Bradley and Illingworth, were notable examples of what can be done by the powder method in analysing a complicated cubic structure. The iron-aluminium superlattices were investigated by Bradley and Jay, the Heusler alloys by Bradley and Rodgers, the nickel-aluminium system by Bradley and A. Taylor, and the chromium-aluminium alloys by Bradley and Lu. Later important work was that on the

ternary alloys and the relation of the lattice structure to the magnetic properties. Professor Bragg took a deep interest in this work on alloys, and it led to a much better understanding of the nature of an alloy and the significance of the different phases, and in this connection there were many helpful discussions with W. Hume-Rothery, who visited the laboratory from time to time. Bradley too spent some time in Sweden in Westgren's laboratory where similar work was in progress.

In 1934 Bragg and E. J. Williams discussed theoretically the effect of thermal movement on the atomic arrangement in alloys, and problems of annealing and kindred subjects, in three papers, one of which formed the subject of a Bakerian Lecture to the Royal Society.

Two Liverpool students, C. A. Beevers and H. S. Lipson, had been working at Liverpool on the structures of the sulphates of beryllium, copper, nickel, and cadmium, and also of the alums, all crystals with water of crystallization, the elucidation of which was an important piece of work, and had been in touch with the Manchester laboratory. In 1935 Beevers moved to Manchester, and continued his work on magnesium sulphate, and Lipson followed in 1936. During 1935 and 1936 they had worked out their method of summing Fourier series, and the wellknown Lipson-Beevers strips were prepared in the Manchester laboratory. Lipson was in due course to succeed W. H. Taylor as head of the Physics Department at the Manchester College of Technology, where he has become well known for his work on optical transforms and their application to structure determinations; and Beevers migrated to Edinburgh, where he has been the centre of an active school of X-ray work.

A feature of the Manchester school during these years was the large number of visiting research students who came to work in the laboratory from all over the world. Among them may be mentioned J. M. Bijvoet, F. W. H. Zachariasen, L. Pauling, B. E. Warren, I. Waller, J. A. Santos, H. Brasseur, F. Machatschki, Sc. Naray-Szabo, H. Strunz, I. Fankuchen, E. Onorato and O. R. Trautz.

Whenever a structure had been determined in the laboratory a model was, if possible, made of it, and various types were fashionable from time to time. In the earlier days, when crystals were still relatively simple, packed spheres often made of dental wax were used. The silicate models were usually constructed by cutting thin glass tubing into lengths equal to the interatomic distances, stringing them together with thin wire to form the structure, and showing the positions of the

atoms, without regard to size, by balls of coloured wax at the junctions of the glass tubing. These models made an impressive show on days when exhibitions of the work of the University were held. They were the trophies of the school, and the memory of them must linger in the minds of all who were privileged to work under Bragg's leadership during those early years.