CHAPTER 18

The Development of X-ray Diffraction in U.S.A.

18.1. The Years before 1940

by Ralph W. G. Wyckoff

The investigation of crystal structure in the United States belongs to two very different periods, a pre- and a post-Second World War epoch. Before this war, and its urgent needs for applied crystallographic information, crystals were investigated for their structure in only a few places, and with one or two notable exceptions this scattered work was carried out with too limited financial support to allow long-range programmes of research. Since the war and the general appreciation of the usefulness of structural information it brought, this situation has drastically improved. We now have vigorous and effective programmes being carried out in many of our better universities as well as in large industrial laboratories; and crystallographic knowledge is being widely accepted as an essential ingredient of modern natural science. Much of this rapid, recent expansion has roots in our earlier, restricted activities and it is with these roots that this preliminary discussion deals.

The concern with crystal structure has never had in America the kind of unity which it has had in Great Britain as a natural outgrowth of W. H. Bragg's early preoccupation with the nature of X-rays. Here the first people to use the experiments of von Laue and the Braggs were interested in specific applications. American physicists dealing with X-rays were not attracted by the possibilities for a new knowledge of the solid state of matter which these X-ray experiments had opened up, and neither were our mineralogists.

To the best of my knowledge, the first American investigations of structure were carried out independently of one another during the period of the First World War. One began at the Massachusetts Institute of Technology, one in the Research Laboratory of the General Electric Company at Schenectady and the third at Cornell. The first two were stimulated by direct contact with the Braggs, the third had a different origin.

In the personal reminiscences of C. L. Burdick (Part VII) we read

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how, after spending some time in the laboratory of W. H. Bragg, he returned to carry through an analysis of chalcopyrite with the help of J. H. Ellis. This was when A. A. Noyes, at whose instigation this X-ray work had been undertaken, was retiring from the Massachusetts Institute to build up a chemistry department in the newly organized California Institute of Technology. Though neither Burdick or Ellis continued to work with X-rays, Ellis remained for some years at the California Institute where he retained an interest in the further development of the subject. The first studies of structure at Pasadena centered around Dickinson who came with Noyes from Cambridge. He carried through a number of structures, partly alone and partly with students. Most of these men did not continue in crystal structure but one who did was Pauling who took over when Dickinson's research interests turned to other matters and whose problems have since determined the pattern of X-ray research at the California Institute.

In his reminiscences (Part VII) Hull recounts how a visit of W. H. Bragg to Schenectady led him to examine the structure of metallic iron and thus through the lack of single crystals to invent the powder method, independently of Debye and Scherrer. He also describes how, having used this method to deduce the structures of many of the commoner metals, he abandoned crystal structure as being a field too remote from the fundamental objectives of the General Electric Laboratory. Davey had, however, been working with him at Schenectady and had there obtained the structures of a number of chemically simple crystals using Hull's powder method. He went to Pennsylvania State College where for the next thirty years he devoted himself mainly to analytical uses of X-ray diffraction, establishing as part of this effort the A.S.T.M. powder diffraction file.

While Nishikawa was a visitor in the department of physics at Cornell, I began under him in 1917 a thesis on the structures of sodium nitrate and cesium dichloroiodide. We had no X-ray spectrometer and our data were drawn from single-crystal photographs, both spectral and Laue, and were interpreted with the aid of space-group theory. Before coming to the United States Nishikawa had used these methods to establish several structures. He had learned of space-group theory from a Japanese professor who twenty-five years earlier had been working in Germany when Schoenflies was developing this theory. Communication with German-speaking Europe was at a low ebb immediately after as well as during the war and we had been using space-group results for several years before becoming aware, through

Niggli's *Geometrische Kristallographie des Diskontinuums*, of a rebirth of European interest in the theory.

On getting my degree I went to the Geophysical Laboratory and thus it came about that of the three original studies of structure in America only one had a continuing existence in a university. In this way the California Institute assumed from the outset a dominant position both as a center of crystal structure research and as a source of trained personel, able, when opportunities later arose, to initiate new centers in other institutions; and the fact that this activity was in the chemistry department is one reason why so much of subsequent crystal structure in this country has been under the sponsorship of chemistry.

Though none served as the basis for a developing school of crystal structure, several physics departments of American Universities were in the 1910's and 1920's actively studying X-rays, and their work has contributed in important respects to the ultimate growth of our subject. Thus Bergen Davis and his students at Columbia were engaged for many years on fundamental problems of X-ray production and its quantitative measurement. Duane's school of X-ray physics at Harvard touched closely on problems of crystal structure. In the early 1920's he became interested in the use of Fourier methods to study the electron distribution in atoms and Havighurst's work with him was a pioneering application of these methods to the determination of electron distributions in the atoms of crystals. Allison is another of Duane's students. And so is G. L. Clark who went to Illinois to become the chief American exponent of applied X-rays. The other American school of that time whose work has strongly influenced the course of crystal analysis was that of A. H. Compton at Washington University and at Chicago. It requires only a glance at his book with Allison to appreciate how much of the quantitative measurement that underlies all modern structure analysis is based on his investigations and those of his school.

Early in the first half of the 1920's there was little extension of crystal structure work in this country. Nevertheless it was during this period that Mc Keehan worked on metallic systems at the Bell Telephone Laboratories and that Davey and Clark began to apply X-ray diffraction to practical problems.

A second stage in the development of crystal analysis in the United States began during the later 1920's and early 1930's with the gradual appearance of more opportunities for research. People to start this new work came from both the California Institute of Technology and from among those who had been gaining experience abroad, mainly with the Braggs. Thus Warren, returning from work with W. L. Bragg, started the investigations in the physics department of the Massachusetts Institute of Technology which he has been continuing ever since. Patterson came via McGill in Canada from a stay in W. H. Bragg's laboratory at the Royal Institution. Also during this period Jette was working on metals at Columbia after being with Phragmén in Sweden. During the 1930's Zachariasen came to the physics department at Chicago from Goldschmidt's laboratory after a stay with W. L. Bragg.

Several workers trained at the California Institute of Technology established laboratories for further X-ray work during this period. Among the more senior of these is Hendricks whose laboratory in the Department of Agriculture dealt for years with the structures of mica and related minerals as well as with problems of electron diffraction. Another is Huggins who has recently retired after many years at the Eastman Kodak Laboratories. More recent people from Pasadena who set up laboratories in the years before the second war are Hoard who went to Cornell, Brockway in Michigan and Hultgren in Harvard, Harker now in Buffalo.

During this period there also sprang up in several universities groups which took their origin less directly from any of the older schools here or abroad. One of these, initiated by F. C. Blake (an earlier student of Duane), was active for several years at Ohio State; Havighurst had worked with him before going to Harvard to study with Duane, and Klug also started with him. Another programme of this period, due to Gruner in Minnesota, seems to have been the first to have been started in the mineralogical department of an American university; for a decade beginning in the later 1920's he studied the clays and other minerals. Ramsdell at Michigan and Pabst at California began working at this time and so did M. J. Buerger, whose work in the mineralogy department at Massachusetts Institute has, however, always reached beyond a preoccupation with minerals.

18.2. From the Beginning of World War II to 1961

by Elizabeth A. Wood

Although publication dwindled almost to nothing during the 1940's because of the war, there was a great deal of crystallographic research going on which was to come to light in a flood of post-war publication.

Neutron Diffraction

Because of nuclear research during the war, neutron beams from atomic piles became available. The phenomenon of the diffraction of a neutron beam by a crystal, predicted by Elsasser in 1936, had been demonstrated in the same year by Mitchell and Powers of Columbia University and by Halban and Preiswerk (reported in Comptes rendus) using a radium-beryllium neutron source.

With the stronger beams from atomic piles, monochromatization became feasible and, with it, quantitative neutron diffraction work on crystals. The horizons opened up by the existence of a set of atomic scattering amplitudes entirely different from those for X-rays (even including negative scattering amplitudes) were quickly recognized by Shull, Wollan, et al. of Oak Ridge National Laboratory and pointed out in such papers as the discussion of NaH and NaD by Shull, Morton and Davidson in 1948.

In addition, the fact that the neutron has a magnetic moment made possible the determination of the arrangement of magnetic dipoles in magnetic materials. Shull and Smart's pioneer work in 1949 at Oak Ridge on the magnetic structure of MnO has been followed by extensive structure work by Henri Levy, W. C. Koehler and Michael Wilkinson at Oak Ridge and also by Lester Corliss and Julius Hastings of Brookhaven National Laboratories.

5f Series of Elements

Another beneficial result of the nuclear research effort was the attention paid by W. H. Zachariasen of the University of Chicago to the 5f series of elements and their compounds. From his research on these substances, there resulted a series of papers in *Acta Crystallographica* extending over 11 years.

Computing Machines

Another important contribution to crystallography traceable to advances made during the war years was the development of powerful electronic computing machines and all their associated automation of data recording, storage and transfer.

In this country one of the first to make advantageous use of this development was R. Pepinsky who in 1947 produced XRAC, the X-ray analogue computer which showed a contour map of the projected electron density on an oscilloscope screen when the Fourier coefficients were set on a system of potentiometer dials. More recently 'programs' have been written which will instruct the various commercially available digital computing machines to do a large assortment of crystallographic chores.

David Sayre in 1945 devised the first least-squares program to be available as a package.

Punched cards came into use in the forties. Effective use of these was made in 1950 by David P. Shoemaker, Jerry Donohue, Verner Schomaker and Robert B. Corey in their three-dimensional refinement of the L-threonine structure.

S. C. Abrahams and Emanual Grison enlisted the aid of the M.I.T. computer *Whirlwind* in the solution of the structure of cesium hexasulfide in 1953 while they were in the Laboratory for Insulation Research at the Massachusetts Institute of Technology.

The widespread sharing of programs that has contributed to the rapid increase in the use of high-speed computers for crystallographic work in the United States is due partly to the personal generosity of individuals who have devised programs and partly to the far-sightedness of the companies who produce the computing machines.

Automatic Data Collection

Automation of computation has inevitably led to automation of data collection. A machine was devised by W. L. Bond and T. S. Benedict in 1955 which will seek rapidly for a reflection and, finding it, record its azimuth and elevation relative to the crystal axes and its integrated intensity.

Subsequently X-ray diffractometers with automatic crystal setting and data recording have been designed by Diamant, Drenck and

Pepinsky of Pennsylvania State University, by J. Ladell of Philips Laboratories and by S. C. Abrahams of the Bell Telephone Laboratories.

Soon such intensity data will be fed directly into the calculating machine and the next contact of the crystallographer with the problem may be his examination of the three-dimensional Patterson diagram!

In the field of neutron diffraction automation is especially important. Because of the long time required to scan a reflection, it is desirable that the diffractometer operate without interruption and without requiring the presence of an operator.

H. A. Levy and S. W. Peterson at Oak Ridge National Laboratory were using an automatic single crystal neutron diffractometer throughout the late 1950's. Langdon, Frazer and Pepinsky described the design of a new type of neutron diffractometer in 1956, and in 1959 Langdon and Frazer published design details of an instrument they had built and tested in which probably the most important new feature was the use of digital angular settings. This instrument has now been modified for tape input and output and made more flexible. Meanwhile, E. Prince and S. C. Abrahams have been using a single crystal automatic neutron diffractometer with paper tape input and output which was designed by them.

Phase Determination

The availability of high-speed computing facilities has made possible the investigation of structures that might not have yielded to the efforts of one individual in a lifetime of old style computation. Partly as a result of the tackling of more difficult structures urgent attempts were made to solve the problem of determining the phases of the various scattered rays which have to be known for a Fourier synthesis of the electron density.

The attempts to use such information as the fact that the electron density is nowhere negative had their first great success in the work of David Harker and John Kasper of the General Electric Research Laboratories in 1948. They applied inequality theorems well known to mathematicians. Although their method has limitations, its publication stimulated thinking on the subject. Subsequent papers pointing out the application of inequalities were published by David M. Sayre and W. H. Zachariasen in 1952, the latter introducing the use of equations that are only statistically true. H. Hauptmann and J. Karle of the Naval Research Laboratory, using the statistical approach and working with joint probabilities concerning several intensities, feel that in this approach lies the true solution to the phase problem. Several structures have been solved with the assistance of the Hauptmann and Karle method but it has not yet come into widespread use.

Patterson Function

The limitations inherent in the Patterson method of vector representation of the data, published in 1934 by A. L. Patterson then at Bryn Mawr College, have not prevented its widespread, almost universal use. Computer programs have made possible the rapid construction of three-dimensional Patterson diagrams. This, along with systematic procedures for extracting the maximum amount of information from the vector representation, will result in even greater use of the Patterson function. This subject has been developed over a period of time by M. J. Buerger of Massachusetts Institute of Technology in a series of papers and in 1959 in a book called *Vector Space*.

It was Dr. Dorothy Wrinch of Smith College who suggested in 1939 techniques which were a powerful aid in deducing the atom positions from a knowledge of the Fourier Transforms of special groupings and their Patterson representations.

'Least Squares' Analysis

In speaking of analytical techniques, the important contribution o E. W. Hughes of the California Institute of Technology should be mentioned. He was the first to introduce, in 1941, the use of the 'least squares' fitting of the data as used by statisticians. In 1946 Hughes and Lipscomb further pursued this attack in applying error theory to least squares analysis.

One of the most powerful computer programs today is a three-dimensional least-squares program devised by W. R. Busing and H. A. Levy of Oak Ridge National Laboratory.

Structure Analyses

The increasing complexity of the organic structures which have succumbed to solution has been mentioned. A plot of their cell content versus year of successful solution anywhere in the world has been published by Jerry Donohue of the University of Southern California. It has a slope of 30 atoms per decade, but every time a new high speed computer comes out, this slope increases. Jerry Donohue belongs to the impressive group of structure analysts that has fanned out in all directions from the California Institute of Technology at Pasadena where the dynamic teacher, Linus Pauling, has inspired the crystallographic research in the Chemistry Department. Beyond this department, Pauling's influence has been widely felt through his book *The Nature of the Chemical Bond* which has had an important effect in stimulating thought on this subject throughout the field of crystallography. Some of his students, such as J. L. Hoard at Cornell, R. E. Rundle at Iowa, W. N. Lipscomb at Minnesota and later at Harvard, and David Shoemaker at Massachusetts Institute of Technology, have established similar fountainheads elsewhere in the country. J. L. Hoard and his students have specialized in complex inorganic structures, including boron and its compounds. R. E. Rundle's group has worked on many inorganic and metallic structures.

Proteins and Related Structures

The concept of the complex spiral structure in proteins introduced by Linus Pauling was an important step toward the understanding of protein structures and resulted in intensified work on this subject at the California Institute of Technology.

During the 1950's David Harker and a small group working with him at Brooklyn Polytechnic Institute concentrated on the protein ribonuclease and related structures. Murray Vernon King of this group developed new techniques for producing, 'staining' and maintaining single crystals of these difficult substances for structure analysis. David Harker and T. C. Furnas Jr., developed the use of the 'Eulerian cradle' for taking complete diffraction data from a single crystal without remounting it, working always in the equatorial zone, a technique of special importance for work on the large-celled organic substances.

Low-Temperature Work

In the middle forties I. Fankuchen and his colleagues developed an 'in-place' method of growing single crystals in a capillary while it was at the center of the X-ray camera by using a regulated stream of cold air together with a heater for remelting undesirable crystals (Kaufman, Mark and Fankuchen, 1947; Kaufman and Fankuchen, 1949; Post, Schwartz and Fankuchen, 1951). W. N. Lipscomb and his school have done pioneering research in low-temperature diffraction work. Some of the early techniques in this field were reported in 1949 by Abrahams, Collin, Lipscomb and Reed. Since 1950, when Collin and Lipscomb published their paper on hydrazine at low temperatures, much work has been done at temperatures down to 78°K, not only at Brooklyn and Minnesota, but at an increasing number of other centers of research.

The work comprises not only determinations of crystal structures of substances liquid at room temperature (Fankuchen, et al., v.s.) and phase-transition studies, but it also holds promise of very accurate structure determinations on substances in which thermal motion presents difficulties at room temperature, that is to say, most substances. Indeed the difficult problems associated with the boron-hydrogen groups whose complexity was pointed out in the decaborane paper in 1950 by Kasper, Lucht and Harker have received much light from the low-temperature structure work done on boron hydrides by Lipscomb and his students. Very low temperatures, in the liquid helium range, have been used by Charles S. Barrett in his studies of metal structures.

Both at Oak Ridge and at Brookhaven single crystal and powder neutron diffraction work has been done at temperatures as low as 1.4°K.

Ferroelectricity and Ferromagnetism

R. Pepinsky, Y. Okaya and others at Pennsylvania State University have without a doubt determined the structure of more ferroelectric and piezoelectric crystals than any other single group. It is not the least of his contributions that Pepinsky has brought to this country many students from all over the world whose interaction with our crystallographers has resulted in mutual enrichment.

Among the other laboratories especially interested in ferroelectric and ferromagnetic crystals has been the Laboratory for Insulation Research at the Massachusetts Institute of Technology where A. von Hippel has directed a series of young research people, many of them visitors from abroad, and the Bell Telephone Laboratories. Of special interest in crystal chemistry and ferrimagnetism as well as for practical applications is the work of S. Geller at Bell on a wide range of crystals with the garnet structure in which the site preference of various ions has been demonstrated.

Electron Diffraction

It was at the Bell Telephone Laboratories in 1927 that C. J. Davisson and L. H. Germer showed that a beam of electrons may be diffracted by a crystal just as an X-ray beam is diffracted, thus demonstrating the wave nature of physical particles and at the same time making available a tool especially valuable for the study of thin surface films and isolated molecules. Germer and his colleagues K. H. Storks and A. H. White proceeded to apply the new tool to the study of the structure of forms of carbon, of soaps and polymers. The folding of polymer chains was suggested in 1937 by Storks to explain the electron diffraction effects he had observed.

The use of electron diffraction for the study of interatomic distances in gas molecules has been the primary interest of Lawrence O. Brockway of the University of Michigan who, particularly in the forties, showed the power of electron diffraction in giving us information about complex organic molecules. His student and collaborator, Isabella Karle, whose husband's work on the phase problem is mentioned elsewhere in this history, has carried on the investigation of molecular structure at the Naval Research Laboratory. Verner Schomaker and his students at the California Institute of Technology, and S. H. Bauer and his students at Cornell have made major contributions to the investigation of gas molecules by electron diffraction.

Because of their shallow penetration, diffracted electrons give us information about the atom layers near the surface of a solid specimen which is not available from the diffraction pattern from the more deeply penetrating X-rays. The extensive, careful research by E. A. Gulbransen of Westinghouse Electric Corporation on thin films of oxides and other tarnishes on metal surfaces has lead to a better understanding of corrosion processes and so has the work of Lorenzo Sturkey of the Dow Chemical Company.

At the University of Virginia, A. T. Gwathmey and K. R. Lawless have used electron diffraction to study the epitaxial relations between surface coatings and substrate metals.

R. D. Heidenreich of the Bell Telephone Laboratories who worked with the electron microscope in its early years of development was a pioneer in 1946 in the use of transmission electron diffraction for the study of thin metal films.

All of these workers and many others who came into the field of electron diffraction from electron microscopy are now using the very powerful selected-area methods which combine electron microscopy and electron diffraction to give detailed structure and compositional information about thin films and surfaces.

The use of very slow electrons, accelerated by a few tens of volts, was early suggested by Germer for the investigation of surface structures and was for many years pursued persistently by F. E. Farnsworth of Brown University who detected the weak diffracted beams with a Faraday cage. Recent investigations using a postdiffraction accelerating technique first suggested by W. Ehrenberg in 1934 are yielding information about the structure of surfaces that are completely free of any foreign atoms and also about quantitatively controlled deposits on these surfaces made possible by present day high-vacuum techniques. L. H. Germer, collaborator in the initial electron diffraction experiment in 1927, is one of the most active investigators in this field today.

Liquids

Short-range order which has been investigated by means of electron diffraction in gases has also been studied in liquids and glasses by means of X-ray diffraction. B. E. Warren of Massachusetts Institute of Technology did some of the early work in this field, perhaps led into it by his pioneer work on the silicates, some of which was in collaboration with Sir Lawrence Bragg. Newell Gingrich, working initially with Warren, has continued his X-ray diffraction studies of liquids at the University of Missouri.

Metals

Recently, B. E. Warren with his many students has been making most careful quantitative analysis of diffraction effects other than sharp Bragg reflections, in particular as they relate to information about lack of perfection in metal structures.

C. S. Barrett of the Institute for the Study of Metals of the University of Chicago has, perhaps more than any other one person, brought X-ray diffraction into the field of metallurgy with his studies of deformation and transformation of metals over a wide temperature range, his investigations of preferred orientation and especially through his book *Structure of Metals* written primarily for the metallurgist.

Because of the widespread practical applications of metals, many of the workers of metals crystallography have emphasized the applied aspect of their work. However, the theoretical approach by Linus Pauling toward giving a unified explanation of known metal structures has stimulated structural research in metals.

Norman C. Baenziger and his students at the State University of Iowa have determined the structures of a large number of intermetallic compounds and alloys with special attention to those involving uranium and thorium.

Teaching

A teacher of many crystallographers at Massachusetts Institute of Technology, M. J. Buerger is perhaps more gratefully regarded by crystallographers for his invention in 1944 of the precession camera than for any of his many other contributions, although the equi-inclination Weissenberg technique introduced by him has also saved hours of distress for many crystallographers. He is one of the editors of the *Zeitschrift für Kristallographie*. A conscientious teacher, he has produced in the last ten years four text books of crystallography and a fifth as co-author. These will be listed below.

X-ray crystallography seems indeed to have reached the text book stage in its fourth decade. The sudden spate of text books has included the following from the United States:

BOOKS

1. Azaroff, L. V. and Buerger, M. J. (Mass. Inst. of Technology): *The Powder Method in X-ray Crystallography*, McGraw-Hill, N.Y., 1958.
2. Barrett, C. S. (Carnegie Inst. of Technology): *Structure of Metals*, McGraw-Hill, N.Y., 1943.
3. Buerger, M. J.: *X-ray Crystallography*, Wiley, N.Y., 1942.
4. Buerger, M. J.: *Elementary Crystallography*, Wiley, N.Y., 1956.
5. Buerger, M. J.: *Vector Space*, Wiley, N.Y., 1959.
6. Buerger, M. J.: *Crystal-Structure Analysis*, Wiley, N.Y., 1960.
7. Clark, G. L. (Univ. of Illinois): *Applied X-rays*, McGraw-Hill, 4th edition, 1955.
8. Compton, Arthur H. and Allison, Samuel K. (Univ. of Chicago): *X-rays in Theory and Experiment*, Van Nostrand, N.Y., 1935.
9. Cullity, B. D. (Univ. of Notre Dame): *Elements of X-ray Diffraction*, Addison-Wesley, Reading, Mass., 1956.
10. Klug, H. P. and Alexander, L. E. (Mellon Institute): *X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials*, Wiley, N.Y., 1954.
11. McLachlan, Dan, Jr. (Stanford Research Inst.): *X-ray Crystal Structure*, McGraw-Hill, N.Y., 1957.
12. Pauling, Linus: *The Nature of the Chemical Bond*, Cornell University Press, 3rd edition, 1960.
13. Zachariasen, W. H. (University of Chicago): *Theory of X-ray Diffraction in Crystals*, Wiley, N.Y., 1945.

Of the books that cannot properly be called text books, two deserve special attention because they are on the desk of every practicing crystallographer. They are R. W. G. Wyckoff's *Crystal Structures* and Donnay and Nowacki's *Crystal Data*. The staggering amount of work that the authors have put into these two books is vastly exceeded by the amount of work they have saved their readers.

A somewhat similar statement could be made concerning the work of the editors of the *Structure Reports* and the *International Tables for X-ray Crystallography* throughout the world. In the United States, C. S. Barrett of the Institute for the Study of Metals and Norman C. Baenziger of Iowa State University have been metals editors for the *Structure Reports* and John S. Kasper of the General Electric Laboratories was one of the two editors of Volume II of the *International Tables*.

The teaching of crystallography in American Colleges may take place in any one of several different departments and some of our best teachers manage to have one foot in each of two departments. In this category we have J. D. H. Donnay, professor of crystallography and mineralogy in the chemistry and geology departments of the Johns Hopkins University, and George A. Jeffrey, professor of chemistry and physics at the University of Pittsburgh.

Rose C. L. Mooney Slater was a pioneer in the teaching of crystallography at a women's college, Sophie Newcomb, Tulane University, and in addition has made important contributions to our knowledge of inorganic crystal structures. A. L. Patterson, who formerly trained crystallographers in the women's college of Bryn Mawr, is continuing to train young men and women at the Institute for Cancer Research in Philadelphia.

Dan McLachlan at the University of Utah, the Stanford Research Institute and now at Denver, has taught with that special sort of imagination and ingenuity that has characterized all of his work.

The teacher whose students are probably distributed in the most heterogeneous assortment of organizations is I. Fankuchen of Brooklyn Polytechnic Institute. This is partly because, in addition to the regular academic courses, he teaches an intensive short summer course for anyone who wants to learn about crystallography. He has taught enthusiastic doctors, dentists, newspaper science writers, high school students, and professors of physical chemistry in medical schools, among others.

Small-Angle Scattering

In 1938, Bernal, Fankuchen and Riley, working in University College, London, described X-ray diffraction measurements of spacings as large as 394 Å by use of techniques involving long exposure of a plate 40 centimeters away from the specimen, the technique later known as 'small-angle scattering'. In this country the technique has been refined by R. S. Bear and O. E. A. Bolduan at M.I.T. as well as by W. W. Beeman and his colleagues at the University of Wisconsin in studies of collagen fibers. I. Fankuchen and his students at Brooklyn Polytechnic Institute have applied small-angle scattering techniques not only to organic substances such as the polyamides, but also to the mineral fibers of chrysotile asbestos.

Minerals

Returning again to M. J. Buerger's laboratory at the Massachusetts Institute of Technology, we see it as a source of mineralogical crystallographers. It was in this laboratory that the structure of tourmaline was determined by Gabrielle Donnay and M. J. Buerger. Gabrielle Donnay has continued in mineralogical crystallography at the Geophysical Laboratory of the Carnegie Institution in Washington. She and her husband, J. D. H. Donnay of the Johns Hopkins University, have enriched the mineralogical crystallographic literature with many papers, both singly and jointly, and the data compilation literature with the book *Crystal Data*. In Washington, too, is Howard T. Evans Jr., also a former student of M. J. Buerger's and now associated with a very active mineral structure group at the U. S. Geological Survey under the leadership of Charles L. Christ. Evans, with the cooperation of M. E. Mrose, has accomplished what is probably the most complete structural analysis of the associated minerals in an ore deposit ever made. Working on the vanadium and uranium minerals of the Colorado Plateau ore deposits, they were able to achieve chemical analysis of the various species by means of structure analysis and by doing so to confirm the genetic role played by weathering that had been postulated by the petrologists.

At the University of California at Berkeley, A. Pabst and his students have studied the structures of thorium silicates and uranothorite.

The wide variety of fields in which X-ray diffraction is now being applied as a tool was emphasized by G. L. Clark of the University of Illinois who in the fourth edition of his book *Applied X-rays*, published in 1957, lists more than a hundred types of industries using powder diffraction in routine industrial analysis. He describes the X-ray diffraction control of the orientation of enormous numbers of quartz crystal oscillator plates as 'the largest scale single-crystal achievement in industry'. The magnitude of the achievement had to do not so much with the number of plates produced as with the development of techniques whereby totally unskilled workers could determine the orientation of a plate to $\pm$ 10′ by X-ray diffraction.

Powder Data Card File

A tool which has greatly aided the use of X-ray diffraction methods in industry is the powder data file jointly sponsored by the American Society for Testing Materials, the British Institute of Physics, and the American Crystallographic Association. It was through the hard work and personal sacrifice of Wheeler P. Davey of the Pennsylvania State University that this file came into existence and persisted through the difficult early years. Now, under the editorship of J. V. Smith, working with special assistant editors for each different crystal field and receiving contributions from large numbers of crystallographers, its usefulness is constantly increasing and receiving wide appreciation.

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Several hundred nonacademic organizations are now using X-ray diffraction equipment. Among these are aircraft companies, hospitals, oil companies, paint manufacturers, museums, steel companies, police departments, glass manufacturers, rubber companies and even gas companies.

One of the most difficult powder diffraction experiments ever to be performed will be attempted in 1963 by William Parrish of the Philips Laboratories. Drawing on his extensive experience in instrument design, he has designed an X-ray diffractometer to be landed on the moon. With the cooperation of Clifford Frondel of Harvard University, the analysis of the data which this instrument will send back to earth may tell us more about the composition of the moon than man has ever known before.

The story of crystallography in the United States would not be complete without an acknowledgment of the important part that visitors from all over the world have played in enriching our crystallographic development. Many have been with us briefly, as André Guinier, Rudolph Brill, John Nye, Victorio Luzzati, Emmanuel Grison and Andrew Lang. Many others have stayed, making their home in the United States, so, for instance Peter Debye, Paul Ewald, Kasimir Fajans, Herman Mark, and William Zachariasen.

Every crystallographer who reads this historical essay will discover grave omissions that have been made. It would be quite impossible to tell the whole story of the extensive spread of diffraction work in the United States.

With our colleagues throughout the world we look forward with confidence to the great achievements that the next fifty years will bring.

Next Section