

*Early Work on X-ray Diffraction in the California Institute of Technology**

LINUS PAULING

The first crystal-structure determinations to be made in the United States were those of Hull, the determination of the structure of some metals by the powder method, and of Burdick and Ellis. The work of Burdick and Ellis was done in Pasadena, in the Gates Laboratory of Chemistry (constructed in 1916) of the California Institute of Technology, which at that time was called the Throop College of Technology. C. Lalor Burdick, after obtaining his M.S. degree in the Massachusetts Institute of Technology in 1914 and his Ph.D. degree in Basel in 1915, had spent a few months with W. H. Bragg in University College, London, learning the technique of using the X-ray ionization spectrometer. In 1916 he built an ionization spectrometer in the Massachusetts Institute of Technology, and then moved to Pasadena, where he built a second one. He and James H. Ellis, who was Research Professor of Physical Chemistry in the California Institute of Technology, then carried out an X-ray investigation of a single crystal of chalcopyrite, 8 mm in diameter. Their paper, published in *J. Am. Chem. Soc.* 39, 2518 (1917), was entitled 'The Crystal Structure of Chalcopyrite Determined by X-rays'. The integrated intensities of 13 forms were measured. The structure was reported to be a superstructure of the sphalerite structure (chalcopyrite is CuFeS_2). The reported structure was almost but not quite right; fifteen years later it was found that the distribution of Cu and Fe among the Zn positions of the sphalerite structure is somewhat different from that proposed by Burdick and Ellis. A paper on the structure of silicon carbide (cubic form) by Burdick and E. A. Owen (Professor of Physics in University College of North Wales, 1926-54, now Emeritus) was published in *J. Am. Chem. Soc.* 40, 1749 (1918). It describes work done by them in London and continued by Burdick in the Massachusetts Institute of Technology.

. Roscoe G. Dickinson came to Pasadena and began his X-ray work

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with the Burdick spectrometer in 1918. In 1920 he received his Ph.D. degree, the first one awarded by the California Institute of Technology; his thesis has the title *I. The Crystal Structures of Wulfenite and Scheelite. II. The Crystal Structure of Sodium Chlorate and Sodium Bromate*. The ionization spectrometer was also used by Richard M. Badger for his undergraduate thesis (B.S. 1921), which has the title *The Effect of Surface Conditions on the Intensity of X-ray Reflections from Crystal Planes*.

Dickinson then began making use of photographic methods. He prepared 'spectral photographs' (rotation photographs) and Laue photographs, and interpreted them by the 'method of Nishikawa (1915) as developed by Wyckoff (1920)'. R. W. G. Wyckoff spent one year, 1921-22, in the California Institute of Technology.

Richard M. Bozorth was the second man to receive the Ph.D. degree from the California Institute of Technology (1922). His thesis contained determinations of the structures of PbMoO_4 (wulfenite), KCN, $(\text{NH}_4)_2\text{SiF}_6$, and CdI_2 , all made with use of spectral and Laue photographs.

X-ray diffraction was for some years the principal field of research in the Division of Chemistry and Chemical Engineering of the California Institute of Technology. By the end of 1922 twenty papers had been published by members of the Division, of which fifteen were on the determination of the structure of crystals. In 1922 structure determinations were published as follows: potassium and ammonium chlorostannate, potassium zinc tetracyanide and the corresponding crystals containing cadmium and mercury, phosphonium iodide, potassium chloroplatinite and potassium and ammonium chloropalladite, by Dickinson; potassium cyanide, ammonium fluosilicate, and cadmium iodide, by Bozorth; and nickel hexammine chloride, bromide, and iodide, nickel hexammine nitrate, zinc bromate hexahydrate, sodium hydrogen acetate, and silver molybdate, by Wyckoff.

Other fields of research began to be prosecuted, and in a few years the papers on the determination of the structure of crystals by X-ray diffraction dropped to about twenty percent of the annual total from the Division of Chemistry and Chemical Engineering, and then to about ten percent, where they remain. Over the period of 44 years since 1917 about 350 papers on X-ray diffraction have been published from the Gates and Crellin Laboratories of Chemistry, representing the determination of the structure of about 350 crystals. Many American X-ray crystallographers received their training in the California Institute of Technology.

I had developed an interest in the structure of crystals before I came

to Pasadena. During the year 1919–20 I had a full-time appointment as Assistant in Quantitative Analysis in Oregon State College. My writing desk was in the chemistry library, and I was thus encouraged to read the journals. When the papers by Irving Langmuir on the electronic theory of valence were published in the *Journal of the American Chemical Society* in 1919 I read them with much interest, and also the paper that Gilbert Newton Lewis had published on this subject in 1916. My interest in the structure of molecules and crystals was awakened to such an extent that in the fall of 1919 I gave a report on molecular structure and the nature of the chemical bond in the research conference of the Chemistry Department of Oregon State College.

In 1920 I re-entered college, as a junior, and in 1922 I received the degree of Bachelor of Science in Chemical Engineering. I was then given an appointment as a graduate assistant in the California Institute of Technology. Professor Arthur Amos Noyes at once wrote to me to advise me about my activities during the summer. I was employed that summer as a paving plant inspector, helping to pave a highway along the Pacific coast near Astoria, Oregon. Professor Noyes pointed out that my training in physical chemistry was not good, and suggested that I work the problems in the textbook *Chemical Principles* that he and Sherrill were publishing that summer. Using the proof sheets of the book, I worked the problems in my spare time. I also read the book *X-rays and Crystal Structure* that W. H. Bragg and W. L. Bragg had written in 1915. The decision was made before I reached Pasadena that I would carry on research in the field of the determination of the structure of crystals by the X-ray diffraction method and would have Dickinson as my supervisor.

When I arrived in Pasadena near the end of September 1922 Noyes suggested that I make a structure determination of the lithium hydride crystal in order to obtain evidence as to whether or not this crystal contained the hydrogen anion. He thought that evidence on this point would be provided by the scattering power of hydrogen for X-rays. I began work on the synthesis of lithium hydride and began the construction of an apparatus to take powder photographs. I gave up the lithium hydride problem shortly, on learning that the structure determination had just been completed by Bijvoet and Karssen.

In the meantime, Dickinson suggested that I also prepare some other crystals for X-ray study. The method that Dickinson and other workers in the laboratory were using had as its first step the preparation of a spectral photography by rotating a rather large single crystal in the X-ray beam from a tube with rhodium or molybdenum anticathode in

such a way as to permit the Bragg reflections from a large developed or ground face to be recorded on a photographic plate (plates, rather than films, were used during the first year or two of my work). The reflections from one face of a cubic crystal gave the edge of the unit cube of the smallest possible unit, the other possible units being integral multiples of this value. A specimen for the preparation of Laue photographs was then made by grinding a thin section of the crystal, usually about 0.3 mm thick, with which several Laue photographs were made. These photographs were indexed by making gnomonic projections. The values of $n\lambda$ for the spots were then calculated for the smallest unit permitted by the spectral photographs and for multiples of this unit. In the preparation of the Laue photographs an X-ray tube with tungsten target was used, with peak voltage 54 kV, corresponding to a short wavelength limit of 0.24 Å. The smallest possible unit for the structure that would account for the reflections observed on the Laue photographs (by giving no $n\lambda$ values less than 0.24 Å) was assumed to be the correct unit. The Laue symmetry of the crystal was found by taking Laue photographs with the crystal oriented in such a way that the X-ray beam was parallel to a principal symmetry axis of the crystal, and the theory of space groups was applied to find all possible arrangements of atoms compatible with the Laue symmetry, the composition and density of the crystal, and the observed X-ray reflections. The effort was made to eliminate all but one of these possible atomic arrangements and to evaluate the parameters determining the atomic positions. Because of uncertainty about the atomic form factors, use was in general made only of qualitative comparisons: when it was observed that one plane gave a stronger X-ray reflection than a second plane with larger interplanar distance it was concluded that the structure factor (with the form factors for the atoms assumed constant) must be greater for the first plane than for the second plane.

This method permitted one or two parameters to be determined rather easily, and more with considerable difficulty. Wyckoff and Dickinson had found that interesting crystals with high symmetry often had structures determined by only one or two parameters, whereas those with low symmetry might involve many parameters. Dickinson accordingly suggested to me that I search the literature for interesting substances that were described as forming cubic crystals and make preparations of them for X-ray investigation. I selected a number of substances, synthesized some of them, grew crystals suitable for X-ray investigation (in general, I tried to grow crystals two or three

millimeters in diameter, in order that I might grind them to obtain a good-sized thin plate for Laue photography), and attempted to determine their structure.

My luck was not good. I made an electric furnace in which anhydrous sulfates could be melted and slowly cooled, and in this way got some nice octahedra of $\text{K}_2\text{Ni}_2(\text{SO}_4)_3$; and on 28 October 1922, one month after my arrival in Pasadena, I prepared a photograph of the spectrum of X-rays from a tube with rhodium target reflected from an octahedral face of the crystal and at the same time, to calibrate the apparatus, reflected from the cleavage face of a calcite rhombohedron mounted just above the other crystal. The spacing for (111) of the sulfate was found to be 5.663 Å, corresponding to 9.808 Å for the side of the unit cube. The density of the crystal, as determined by the pycnometer method, was 3.33 g/cm³, corresponding to four formulas per unit cube. A Laue photograph made on 31 October 1922 showed the symmetry expected for point group T or T_h , and also showed no reflections requiring the unit to be larger than 9.8 Å on edge. The space group is T^4 . This space group has positions for four equivalent atoms, with one parameter, or twelve equivalent atoms, with three parameters. Hence there is one parameter for every four atoms in the unit cube. There are 76 atoms in the unit cube, and the structure is accordingly determined by 19 parameters. I at once decided to work on another crystal. (By study of an isomorphous crystal, langbeinite, $\text{K}_2\text{Mg}_2(\text{SO}_4)_3$, this structure has recently been determined.)

I then decided to attack an intermetallic compound. No structure determination for an intermetallic compound had yet been made, and as an undergraduate I had been interested in metallography and had at one time considered the possibility of specializing in the chemistry of metals and alloys. A search of the literature revealed that big single crystals of a cubic compound of sodium and cadmium, NaCd_2 , could be prepared by dissolving cadmium in an excess of molten sodium and allowing the melt to cool slowly; on treatment with absolute ethanol the excess sodium could be converted to sodium ethanolate, leaving large octahedra of the intermetallic compound. In this way I obtained fine crystals about three millimeters in diameter. I made X-ray photographs of one of these crystals in November 1922, and found that the unit cube is about 31 Å on edge and contains about 400 sodium atoms and 800 cadmium atoms. I did not know how many parameters would be required to determine its structure, but it seemed evident that I should attack some other crystal. I have returned to the study of NaCd_2 from time to time, and other X-ray crystallo-

graphers have also investigated it, but its structure is still unknown.

My third effort was with cubic crystals of CaHgBr_4 , which are easily grown from aqueous solution. The cubic unit was found to have edge 19.14 Å and to contain 32 atoms of calcium, 32 of mercury, and 128 of bromine. This crystal, too, seemed to be too complicated for successful attack at that time. The structure has not yet been determined by anybody.

Dickinson then proposed that a mineral be investigated, and he selected molybdenite. He cleaved a section about 0.3 mm thick from a chunk of the mineral, available in bulk in the chemistry stockroom. Excellent X-ray diffraction patterns were given by this cleaved section and the structure determination was carried out in a month. This structure involves one parameter.

I then attacked several other crystals with success. In particular, another intermetallic compound was prepared and was found to have a simple structure. This compound, with formula Mg_3Sn , was made by melting together the metals in the proper ratio and allowing the melt to cool slowly. The compound is brittle, and by striking the solidified mass with a hammer it was broken into fragments, which were found to be single crystals bounded by octahedral cleavage faces. The structure is that of fluorite.

During the following decades more and more powerful methods of crystal analysis have been developed. Each year brings many interesting reports about new structures, with novel features. I think, however, that none of them causes in me such a feeling of pleasure as was produced by the successful determination of the structure of molybdenite and the discovery that the six atoms of sulfur are arranged about the molybdenum atom at the corners of a trigonal prism, rather than of the octahedron characteristic of sodium chloride and some of the other simple structures known in 1922. (For some reason that I do not remember, but that may have been my feeling of astonishment about the sizes of atoms, the coordination polyhedron is described in the paper that Dickinson and I published on the structure of molybdenite as a 'small' triangular prism.)

Forty years ago very few structures had been determined. Any crystal that could be successfully attacked had a good chance of giving a surprising result. Now many structures have been determined, and we know a great deal about structural principles; but we do not know everything, and the X-ray crystallographer, as he carries out the study of another crystal, still has a good chance of being surprised by the result of his work.