A. W. Hull

Drs. Hull and Burdick, both intimately connected with the first attempts in the United States to carry out crystal structure analysis by the use of x rays, recall their experiences of four decades ago in the two pages that follow. The introductory note appearing below was written by Edward W. Hughes, research associate in chemistry at the California Institute of Technology.

C. L. Burdick

X-RAY CRYSTALLOGRAPHY

THE electromagnetic wave nature of x rays was first firmly established in 1912 by the observation of diffraction of x rays by crystals in the famous investigations of Friedrich, Knipping, and von Laue.[1] The application of x-ray diffraction methods to the determination of the detailed structure of crystals was demonstrated within less than a year by W. L. Bragg[2] and since that time literally thousands of papers have appeared describing either improvements in these methods or giving the results of their application to crystals, the natures of which have become increasingly complex as newer methods of increased power have been developed.

Perhaps because of the war which began in Europe in 1914, it was nearly four years before any results based on the new discovery were published in the United States. The first experimental work began in 1916 and the first papers were published in 1917.

In the Research Laboratory of the General Electric Company in Schenectady, Dr. A. W. Hull independently discovered the powder method of crystal-structure investigation and used it to work out the atomic arrangements in many metals. His results were first presented orally to the American Physical Society in 1916 but the first published abstracts [3] appeared in 1917 and the first full paper [4] somewhat later in the same year.

In the meantime, stimulated by the encouragement and support of A. A. Noyes, experimental work employing the single-crystal methods of the Braggs was started late in 1916 in the new Gates Laboratory of Chemistry at the California Institute of Technology in Pasadena by C. L. Burdick and J. H. Ellis. They soon determined the structure of the mineral chalcopyrite, the result appearing in two papers [5] in 1917.

To commemorate the fortieth anniversary of these pioneering works a one-day meeting of x-ray crystallographers was held at Pasadena on December 16, 1957, by the California Institute of Technology, using funds provided by the Lalor Foundation. About fifty scientists attended. There were eleven contributed papers dealing with various aspects of crystal structure research, representing achievements in eleven different laboratories in the United States, England, and the Netherlands. In a longer invited paper Dorothy Hodgkin of the Chemical Crystallography Laboratory, Oxford University, described the work of the group under her supervision which resulted recently in the full determination of the very complicated structure of the molecule of vitamin B_{12}. Thus the work of the American pioneers was contrasted with the most difficult and complicated application of these methods successfully completed to date.

In the evening there was a dinner after which Professor Pauling read a communication from Dr. Hull, who was unable to attend, and introduced Dr. Burdick (the only survivor of the Pasadena workers) who gave an account of the early days of x-ray crystallography both abroad and in the Gates Laboratory. The stories by Doctors Hull and Burdick have been written down by them and appear herewith.

1 Friedrich, W., Knipping, P., and Laue, M. von, Ber. bayer. Akad. Wiss. (Math.-phys. Kl.) 303 (1912).
2 Bragg, W. L., Proc. Roy. Soc. (London) **A89**, 248 (1913).
3 Hull, A. W., Phys. Rev. **9**, 84 and 564 (1917).
4 Hull, A. W., Phys. Rev. **10**, 661 (1917).
5 Burdick, C. L., and Ellis, J. H., Proc. Nat. Acad. Sci. **3**, 644 (1917); J. Am. Chem. Soc., **39**, 2518 (1917).

An Account of Early Studies at Schenectady

By ***Albert W. Hull***

MY work in electronics was interrupted for several years by a lecture by Sir William Bragg. Sir William was in this country early in 1915, and we invited him to speak at our colloquium. He told us about his new work on the study of crystal structure by means of x rays. At the close of the lecture, I asked him if he had been able to find the structure of iron. He had told us about some structures, sodium chloride and copper and a few other materials that he had successfully analyzed. His answer to my question was typical of him. He might have said, "No, but we think we'll have it very soon."

Instead of that he answered very simply, "No, we've tried, but haven't succeeded."

Well, that was a challenge—such a challenge as a young man needs—and I decided that I'd like to try to find the crystal structure of iron, reasoning that it might throw some light on the fact that iron is a magnetic material. I made this decision in spite of the fact that I was almost totally unfamiliar with either x rays or crystallography.

Almost immediately, therefore, I began getting apparatus together to do x-ray crystal analysis research. I decided to use direct current for this study in order to make more precise measurements. We had available the new Kenotron rectifiers, which our laboratory had just developed, to rectify the alternating voltage.

It was necessary to smooth out the fluctuations of this rectified voltage, which I did in the way that any physicist would do, by using a pair of condensers across the line with an inductive choke between them. I had no idea of making an invention and when a young patent attorney, Mr. W. G. Gartner, who was following the work of the Laboratory for the General Electric Patent Department, came to see me to see if there was anything patentable in my apparatus, I told him, "No." But in looking it over, he noticed this filter circuit and patented it for me. Ten years later I was surprised to learn that this filter circuit was used in all broadcast receiver circuits, and that every receiver manufacturer in the country was licensed under my patent.

Bragg's x-ray crystal analysis had been done with single crystals, mounted so that they could be rotated to expose one face or set of crystal planes at a time at the reflecting angle for the single x-ray wavelength used. Since single crystals of iron were not available, I decided to try using a crystalline powder, reasoning that I would obtain reflections from all planes at once, and might be able to unscramble and identify them.

An interesting incident occurred in the early experiments with this method. I got some good diffraction patterns of iron powder quite early. But being still busy with dynatrons, I turned them over to an assistant to calculate on the basis of Bragg's formulae, to see whether they were consistent with any of the simple cubic structures. This young lady was quite able, but she made a mistake and reported that they were not consistent with any cubic structures. I proceeded to work with some other materials for the time being. Eventually, with the help of Dr. Frederick E. Wright, of the Geophysical Laboratory in Washington, who visited me for a couple of weeks, I got some data with a single crystal of silicon steel, about three and a half percent silicon, which we guessed would have a structure similar to iron. We found that it had a body-centered cubic crystal structure.

Immediately I wondered why my original data for iron were not consistent with this structure. While riding home on my bicycle for lunch, I went over the data in my head and made the calculation, and I discovered that these original data were correct, and were consistent with a body-centered cubic structure for iron.

I published this work on x-ray powder diffraction in 1916. In the meanwhile, Debye and Scherrer had been working in this field at the University of Göttingen in Germany. This was during the war, and we got no journals from Germany. After the war was over, I discovered that they had developed just the same method and had published it earlier than I did, by several months, so this method is quite properly called the Debye-Scherrer method of crystal analysis.

As a philosophical afterthought, I must admit that the reason I was so late was that I had continued to be interested in the application of the dynatron. I was trying to develop the dynatron as an amplifier, with some success. That is why, instead of making the calculations about the iron crystals myself, I turned them over to an assistant. The philosophy behind that incident, which is typical of all the experience I've had, is that whenever I've been diverted into spending time on development, it turned out to be a poor investment of time. My advice to any true scientist who is interested in science and not in engineering is not to worry about the applications of what he discovers but to go on to discover something more.

Research at General Electric was interrupted by the war, our laboratories devoting all their energies to a study of the submarine detection problem.

After the war, I returned to x-ray crystal analysis and soon had analyzed all the easily available metals and other common elements. I might have gone on indefinitely analyzing more and more substances, but I got a little feeling from Dr. Whitney's attitude—he wouldn't advise me—that I had gone far enough. Dr. Langmuir advised me that there was no end to it, and that I could do something more interesting. So I dropped the crystal-analysis work and went back to electronics.

The Genesis and Beginnings of X-Ray Crystallography at Caltech

By ***C. L. Burdick***

THAT Caltech was one of the first two centers in America where x-ray crystallography was started and continued was due entirely to the imagination, vision, and conviction of Dr. Arthur A. Noyes. In 1916, which was very early in Caltech's beginnings, Dr. Noyes was nominally visiting professor of chemistry, but actually he, with Drs. Millikan and Hale, was planning and shaping the future of this whole great institution. This particular specialty was only one of the many in which he saw great promise and forthcoming utility.

Prior to 1915 Dr. Noyes was occupied wholly as director of the Research Laboratory of Physical Chemistry at MIT in Boston, and it was there in 1913–14 that I came to know Dr. Noyes and to be a graduate student under him at the laboratory in MIT's old "Engineering C" building. This was near the end of the halcyon days of classical physical chemistry when on the staff could be noted among the younger men such names as G. N. Lewis, C. A. Kraus, and F. G. Keyes.

Dr. Noyes encouraged me to go abroad for doctorate work and postdoctoral study, and it turned out that I sailed from New York in July 1914 on the last regular German liner to get through to Hamburg. Because of war conditions my doctorate period was divided between Professors Fichter and Rupe in Basel and Professor Willstätter at the Kaiser Wilhelm Institute for Chemistry in Berlin-Dahlem. It might be noted that there were then two young, comparatively unknowns by the names of Hahn and Meitner in this same Institute. Following this, the writer had a brief period of postdoctoral work at the Kaiser Wilhelm Institute of Physical Chemistry under Professor Fritz Haber and then a later opportunity to work on "Reststrahlen" with Rubens at the University of Berlin and to sit in on the lecture courses of Nernst, Planck, and Einstein. What untold recognition and appreciation these names call forth today.

Early in 1916 it was only with some circumlocution, occasioned by the separate British and German censorship of all mail from America, that advice came to me from Dr. Noyes to try to find a way to spend my last months abroad working in the x-ray laboratory of Professor William H. Bragg at University College in London. In his letter Dr. Noyes expressed his strong belief in the importance of x-ray atomic structure analysis for the future of theoretical chemistry, and his wish to get something of the kind started at MIT.

It was not so simple for an impecunious, young PhD of American neutrality without connections to get from Berlin to London during the critical period of the Zeppelin raids and unrestricted submarine warfare. But due to the volunteered help and influence of Professor Kamerlingh Onnes of the Cryogenic Laboratory in Leiden, it was accomplished.

The six months in the laboratory of Professor Bragg were of inestimable value, even though its leader was largely occupied with war work. With what time Dr. Bragg had to spend with us in guidance, Dr. E. A. Owen and the writer were able to work out a tentatively satisfactory x-ray structure for carborundum, which was later published.

An interesting presentation could be made of the primitiveness of the equipment then available, the old-fashioned induction coil with Leyden-jar condensers and a mercury interruptor, the gas-filled x-ray tubes of unpredictable and uncertain output and "hardness", and gold-leaf electroscopes with the strangest static aberrations when it came to measuring ionization intensities.

On returning to MIT, which was in process of moving from Boston to Cambridge, my assignment from Dr. Noyes was to build a Bragg x-ray spectrometer with any improvements which the state of the art would permit. This meant, first, having at hand a really good x-ray transformer with rotary-disc rectifier and secondly, and of most importance, an only just then developed, new Coolidge x-ray tube fitted with a palladium target. Dr. James A. Beatty, then a student, was principal collaborator in building, putting this machine into initial operation, and testing.

In the latter part of 1916 when Dr. Noyes left for his annual tour of duty as visiting professor at Caltech he asked me to go with him and build another spectrometer embodying the refinements which our tests had shown could be made. The Caltech team on this was James H. Ellis, Fred Hensen (instrument maker), and myself. The things which made the original Caltech spectrometer probably the best of its day were its high-power input and relative constancy of measured electrical energy to the tube. This gave possibilities for narrower spectrometer slits, precise angle measurements, sharp reflection peaks, and better measurement of relative reflection intensities of the spectral orders than had probably ever been made before.

The measurements carried out in these months permitted the determination of the crystal structure of chalcopyrite and resulted in two papers by Ellis and Burdick. These were submitted to the *Journal of the American Chemical Society* and the *Proceedings of the National Academy of Sciences* early in 1917, and appeared as publication Number 3 of the Gates Laboratory of Chemistry.

Then the United States entered the war, Dr. Noyes' time was spent in large measure in Washington, Burdick was called from the US Ordnance Reserve into the nitrogen fixation program, and for a time the x-ray crystal work at Caltech lagged. After the war, with the arrival of Dr. Roscoe G. Dickinson, the wheels hummed again. High-voltage sparks flew and research results by many collaborators came out apace. Today the successorship of Dickinson is in the notable hands of Pauling. Dr. Noyes' vision of the early days of 1916 has paid off and will continue to do so in generous measure.