Personal Reminiscences

B. E. Warren

It would be very interesting to know the extent to which chance occurrence leads people into the field which they follow for their life work. While I was a student at the Massachusetts Institute of Technology, Professor Max Born made a short visit, and gave a set of lectures on Crystal Lattice Dynamics. I probably did not understand one quarter of what he said, but nevertheless the set of lectures started an interest in crystal physics.

Having been awarded a small fellowship for a semester in Europe, I chose Stuttgart so as to combine the X-ray diffraction course of Professor Glocker with theoretical work under Professor Ewald. On arrival at Stuttgart, I was quickly sized up as a completely inexperienced individual, and assigned a little problem calculating the indices of refraction of a salt whose structure was at that time in doubt. The calculation was to be done by the method developed in Born's *Atomtheorie des Festen Zustandes*, and I was left to dig it all out by myself. This might sound like fiendish treatment of an innocent young student (and it was), yet I have always felt a deep debt of gratitude to Paul Ewald because he gave me exactly what I needed most at that time. The calculation was of no importance, but what I took away from Stuttgart at the end of the semester was a feeling of confidence, having dug out this small problem completely on my own, I would not hesitate to tackle any subsequent problems. It is generally true that the best teaching is the kind that forces a student to teach himself, and thereby learn to think for himself.

Back at the Massachusetts Institute of Technology as a graduate student, there came another and extremely important chance occurrence. Sir Lawrence Bragg spent four months as a visiting professor giving a set of lectures on X-ray diffraction and crystal structure determination. For his lectures Professor Bragg needed crystal structure models, and since these were not available it was necessary to make

Contents

them in a hurry. I was lucky enough to win the opportunity to be Professor Bragg's chore boy in charge of building models in a hurry. Since this involved a great deal of discussion and planning, it was an opportunity to get acquainted with Professor Bragg.

As is well known the really great men of the world are friendly, considerate, and completely devoid of pretension. One day Professor Bragg dropped the remark that being entertained and invited out to dinner nearly every night in the week was rather strenuous and tiring. So with the naiveness of youth, I promptly asked if he would like a change such as going to the hockey game that night between the Canadian Mapleleafs and the Boston Bruins. He eagerly accepted and we went, and it was an evening which I shall never forget. First he had to know which was the home team, and from then on he cheered as loudly and enthusiastically for the Boston Bruins as any Bostonian in the audience. Another time were we taking a Sunday hike in the mountains of New Hampshire. After a long hike in the snow we built a camp fire to cook the hot dogs which we had planned for lunch. On opening the packsack, I found that I had brought the rolls but had forgotten the dogs (frankfurters). Professor Bragg still laughs about this when I meet him, he had never supposed that any person could have a face as long and sad as mine when the awful discovery was made.

In addition to building models during these four months, I had the opportunity to work with Professor Bragg on the structure of diopside. An excellent set of quantitative intensity measurements had been made by West, and Professor Bragg had brought the data with him. This was my first contact with structure determination and I probably learned more in those four months than in any other period. It was an exciting experience, diopside was the first of the chain silicates, and the chain structure was completely unexpected.

A year or two later I had the opportunity to spend a few months at the University of Manchester. This was in one of those golden age periods, the membership of the laboratory including names such as Professor Bragg, James, West, W. H. Taylor, Bradley, Ito, Wood and Zachariasen. There was an opportunity to work for a while under James. I imagine that most people who have worked under this great man have had the same experience, it is not until some time later that one begins to realize how much he learned from working with James. At this time complex silicate structures were being done by quantitative intensity measurements using a spectrometer with ionization chamber and electrometer. The crystal was turned in steps to the beat of a metronome, while the electrometer deflection was held at zero by varying a balancing voltage, an operation which required a certain amount of manual dexterity. Present day students who are brought up to think that all experimentation must be done by completely automatic apparatus, would probably be horrified to think of working in this way, and they would probably have trouble in believing that really excellent measurements were made like this in the early days.

After Manchester I settled down at M.I.T. to work on complex silicate structures. This was the period when structures were done with a set of rotation and oscillation patterns. From the cell axes, the space group, and the laws of silicate chemistry, it was usually possible to guess the few likely atomic arrangements. The correct values of the coordinates were then obtained by adjusting the values until there was good agreement in relative intensities for a large number of spots on the oscillation patterns.

Although not yet realizing it, my real interest was in the physical optics of X-ray diffraction and not in structure determination. A chain of events soon brought me into a new field of research. Zachariasen's famous paper suggesting the random network structure of inorganic glasses was of great interest because of my familiarity with silicate structures. Debye's treatment of diffraction by gas molecules, and the Fourier inversion of liquid patterns outlined by Zernike and Prins and applied by Debye and Menke, suggested the possibility of X-ray studies of a non-crystalline material such as glass. This started a programme on the X-ray study of the structure of glass which lasted several years. Crystal monochromated primary beams were just starting to be used, and intensities were measured by film recording and microphotometering. Problems of technique such as the quantitative measurement of diffuse intensities, and the Fourier inversion of diffuse intensities, which were encountered here for the first time, have run through a great deal of the later work in other fields.

An interest in graphite and carbon black started at this time in a purely accidental way. The Fourier inversion method was being applied to the diffraction patterns of glass, and it seemed desirable to try the method out on other forms of amorphous matter. Knowing nothing about carbon black except that it was supposed to be an amorphous form of carbon, an X-ray recording and Fourier inversion was carried out on a sample of carbon black which happened to be in the laboratory. It turned out of course that carbon black is an extremely interesting material with its transition from the amorphous to the crystalline state through the two-dimensional random layer structures. The name 'turbostratic' which has come to be applied to this type of random layer structure was coined by my friend the chemist Nick Milas. Since he is a very competent Greek scholar, I asked him to coin a word for me from the Greek, but after some consideration Nick reported that this job could be handled better from the Latin.

I had never had any interest in metals until the idea occurred that short-range order in binary alloys should produce a modulated diffuse intensity from which the short-range order parameters could be obtained by a Fourier analysis. It was an obvious extension from the diffuse intensity of an amorphous material to the diffuse intensity which results from disorder in a crystalline material. Order-disorder in binary alloys has turned out to involve many interesting problems in technique and in the physical optics of diffraction by imperfect structures. The subject has suggested a large number of measurements and experiments, but curiously enough each investigation seems to open up new problems and indicate new complexities. It sometimes seems as if the study of order-disorder in binary alloys is like climbing a mountain where for each meter we rise in altitude, the peak goes up by two meters, so that although we are making great progress the end of the climb gets ever farther away.

Throughout the fifty years which we are reviewing, X-ray diffraction has never run out of problems, because each problem attacked introduced new questions which needed to be answered. Rather early in the study of short-range order in alloys it turned out that the correction for temperature diffuse scattering was the principal limitation to the accuracy of the short-range order parameters which could be obtained. Hence a study of temperature diffuse scattering was undertaken with the sole idea of learning how to correct for what was a nuisance in the measurement of short-range order parameters. But Laval and James had already shown that measurements of the temperature scattering of X-rays could be used to obtain the spectrum of the elastic waves which constitute the thermal vibrations in a crystal. And so it turned out that the temperature scattering was more than a nuisance, it was of great interest in itself as a method for determining the elastic spectrum of crystals. This seems to be part of the general principle that most experimental nuisances are potentially important tools for the study of some other effect. The nuisance results from some physical effect and it is therefore a means for studying this effect, furthermore the effect is big enough to measure otherwise it could not be a nuisance.

In recent years the work of my laboratory has been largely devoted to the study of imperfections in structure, such as the imperfections resulting from cold work in metals. Diffraction in a cold worked metal presents some very interesting problems in the physical optics of diffraction, and this was surely the motivating reason for going into this field. This last change is probably in line with a general trend in the application of X-ray diffraction, and in our point of view concerning the crystalline state. In the early days we tended to think of crystals as having perfectly repeating structures, and the interest was wholly in the determination of this ideal structure. Today we realize that there are many kinds of imperfections in crystals. For many physical properties it is the imperfections that are of primary importance, and hence a great deal of present day interest is centered around the X-ray studies of the imperfections in crystals.