Recollections of Dahlem and Ludwigshafen

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In 1921 there were essentially three groups in Berlin-Dahlem which worked in the X-ray field: Becker and Jancke who were associated with Professor Herzog; Böhm and Zocher who cooperated with Professor Freundlich, and Brill and myself who worked with Polanyi and Weissenberg.

At that time the theory of X-ray diffraction was as good as completely developed in a series of important contributions beginning with the original articles of M. von Laue and W. H. Bragg and culminating in the dynamic theory of P. P. Ewald, which described the interaction of an X-ray beam with a crystal lattice in all details. From the experimental point of view, however, the field was still in a rather infant state. There were no X-ray tubes available which could be operated at high intensities over longer periods without permanent careful supervision, there did not exist precision cameras in which crystals or crystalline objects could be conveniently mounted for irradiation in all possible orientations and there were no instruments designed which would permit X-ray diagrams to be taken at extravagant conditions such as at very low or very high temperatures, in a vacuum or in an atmosphere of a chemically very reactive gas. As a consequence most structure determinations prior to that time either operated with well developed single crystals (mostly of inorganic nature) or with polycrystalline powders of relatively simple structure (elements or compounds having lattices of high symmetry). The groups in Dahlem, however, were interested in colloidal systems of inorganic nature, in organic substances, most of which form crystals of low symmetry, and in polymeric materials, which represented a class of organic compounds that was rather unexplored at that time. The main concern of all of us

* Since the author of this review has been previously connected with a large part of this work from 1921 to 1931, it is a special pleasure for him to follow Prof. Ewald's suggestion in giving a brief account of the activities during this period.

Contents

was, therefore, to improve our experimental procedures and the evaluation of the data in all possible ways.

A first important step in this direction was the development of the techniques of fiber diagrams and, in general, of diffraction patterns of very small crystals having some degree of orientation in space. Polanyi and Weissenberg opened the way for this approach by a careful and exhaustive analysis of the way in which spatial order inside of a sample reflects itself in spatial order of the diffraction points on the photographic plate and a series of papers on materials of all kinds utilized their formulas for the elucidation of the deformation of metals, of the growing of colloidal suspensions and of organic crystals, and of the basic structure of natural fibers, such as cellulose and silk. One interesting result was that the crystallographic elementary cell of cellulose and silk was found to be very small. This led Polanyi and Brill to the conclusion that these materials are either built up by small cyclic units or by long chains, which pass in a continuous manner through a number of consecutive unit cells.

These early results of the Dahlem X-ray group have later been often quoted in an incorrect manner by assuming that the X-ray diagram of cellulose and silk was an indication of a low molecular weight of these materials.

Another important area of improvement was the construction of X-ray tubes which would permit to obtain monochromatic radiation (mostly Mo, Cu, Fe, or Cr) of high intensity (10–100 mA) at moderate voltages (30 000–60 000 volt) by a more or less automatic operation so that these tubes could either be run at peak intensities for a short time or at moderate intensities over long periods. It took several years and the combined efforts of our best experimentalists (Brill, Boehm, Ehrenberg and von Susich) to arrive at a situation where strictly monochromatic diagrams of normal samples could be made in a few seconds and, correspondingly, very small specimens could be X-rayed within reasonable times of exposure. As a consequence, the structure of B_2H_4 was determined from powder diagrams of the crystallizate of less than half a cubic centimeter of the gaseous materials at $-180°C$ by Pohland and the atomic weight of hafnium was computed by Hassel from the dimensions of the unit cell and the density of a $(NH_6)_3HfF_7$ single crystal which weighed only 0.2 gammas. Relatively fast chemical reactions, such as the alkalization of cellulose and the hydration of certain silicates were cinematographed by Katz, Rosbaud and Susich and the rapid phase change during the crystallization of rubber was quantitatively studied by Hauser.

But the ease with which X-ray patterns could be obtained in short times even under somewhat extravagant conditions (temperature, vacuum, pressure, chemical environment) led not only to interesting results in many special cases, it also produced an important change in the general use of this technique. Until then, the preparation of a good and clear diagram was a relatively difficult experiment which required considerable skill, time and effort. Hence, it was customary to use one or two X-ray patterns as the basis for a scientific paper and to evaluate these diagrams in all possible directions with the aid of assumptions which were not always absolutely justified. Now the X-ray method became one of the standard analytical tools, which was used to check almost as with a microscope, the progress of a scientific investigation step by step, with the aid of orienting snapshots, which were most valuable to pin down the situation and to help decide the next step of the work. For example more than fifty individual diagrams were made during a study of the swelling of cellulose by Katz, but only the five or six best ones were actually included in the publication; almost one hundred orienting pictures were made by Polanyi and Schmid in their systematic studies of deformation mechanism of single metallic crystals. This diagnostic use of the X-ray method as an infallible guide in solid state research of all kind is taken for granted today but it needed considerable skill and effort to develop it during the years from 1923 to 1928.

One of the most valuable products of this era was the *X-ray Goniometer* which was conceived and constructed with all its details by Weissenberg and first put to practical use by Boehm. Even the most recent instruments of this type are not much better than the first original Weissenberg camera which is still in use in the laboratories of the Fritz Haber Institute in Berlin-Dahlem. Other important instrumental innovations which have greatly contributed to the usefulness and applicability of the X-ray method were cameras for exposures at very low and very high temperatures, in vacuo and under pressure, furthermore crystal monochromators with flat and curved crystal plates, automatically recording ionization chambers and arrangements to produce highly parallelized and very intensive beams of a diameter down to a few microns (Kratky's micro X-ray camera).

For several years (1921–1924) the interest in structure determinations prevailed, but then the key role of X-rays and gamma rays for basic problems concerning the structure of radiation and matter (Compton effect, Geiger counter, light quantum hypothesis,

dispersion theory) focussed attention on general questions of the physics of X-rays and electrons. Fortunately the highly developed technique of producing and registering strictly monochromatic and parallel X-ray beams was exactly what was needed for successful experiments along these more fundamental lines. Thus under the influence and with the active cooperation of Einstein, Kallman, von Laue, Szilard, and Wigner studies on the width of X-ray lines, the anomalous dispersion of X-rays, the intensity, width and polarization of the Compton lines, and on polarization of characteristic X-ray radiation were carried out and published in a series of articles. Equally fundamental was a thorough test of Ewalds' dynamic theory with the aid of very careful and delicate precision measurements of the angular width of X-ray reflection, which was carried out by Ehrenberg, together with Ewald and Mark. In connection with this work another instrument was developed—the double crystal X-ray spectrometer—which kept on playing an important role in precision measurements of high energy spectroscopy until now and was recently improved and refined for the use with gamma rays by Jesse Dumond and Hans Mark.

In 1927 the author and part of the Dahlem group moved to Ludwigshafen on Rhine and attempted to introduce X-ray diffraction methods into the realm of industrial application. With the cooperation of a few new members several problems of practical importance were attacked but fundamental studies in the field of X-ray and electron physics were not neglected. Dohse, Dunkel, Hengstenberg, Wierl, and Wolf made interesting contributions to the nature of the adsorbed state of small organic molecules on solid surfaces, the mechanism of deformation of crystals, the scattering of electrons by simple molecules in the gaseous state (Wierl) and the adsorption of light by coloured organic substances. The techniques for the preparation and registration of intense monochromatic beams of X-rays and electrons were further improved, and K. H. Meyer initiated work on the establishment of a uniform picture concerning the molecular structure of high polymeric material and synthetic substances.

In the laboratories of the I. G. Farbenindustrie A. G. in Ludwigshafen the method and reasoning of solid state physics had to be applied to the characterization and testing of industrially important materials in competition with the already well known and firmly established classical procedures of inorganic and organic chemistry. These branches were in the hands and under the supervision of highly qualified industrial experts such as Alwin Mittasch and Otto Schmidt and had proven their usefulness and indispensibility in many cases.

The new group had to demonstrate its own value for the company in the face of many existing strongly entrenched working teams. This was a difficult position and not even the benevolent and continuous support of such inspired industrial leaders such as Bosch, Gaus and K. H. Meyer would have prevented a gradual starvation of the new approach. Fortunately, however, there were some early successes which convinced even the most skeptical observers that the new methods and the new atmosphere, which they carried with them into the somewhat stagnant air of the great plant were of undeniable value and almost necessary for a successful progress in the future fields of chemical technology. Brill demonstrated convincingly the value of X-ray analysis for the study of catalysts in the ammonia and methanol synthesis. Susich and Valko were able to characterize synthetic fibers and rubbers with X-ray and electron diffraction far easier and better than anyone else in the wide-spread industrial organization of the I. G. Farbenindustrie. Dohse and Dunkel made substantial contributions to the understanding of polymerization reactions and Wierl and Wolf surprised the dyestuff experts by showing them how much they can learn about the objects of their interests and efforts by the use of X-rays and electrons. Practical people are slow in acknowledging the value of new approaches but very fast in using them extensively once their value has been established. As a consequence it took only four years and the modern methods of spectroscopy, scattering and photographing with X-rays and electrons were a part of process and product control not only in Ludwigshafen but also in most other plants of the Company.