Ninety Years of Powder Diffraction: from Birth to Maturity

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The expression "powder diffraction" denotes the phenomenon of diffraction of any electromagnetic waves or particles on polycrystalline (powdered, bulk or thin film) materials which is used in a wide variety experimental settings. The X-ray powder-diffraction method was devised and developed during the First World War (1916) by a Dutch/Swiss team, Peter Debye and Paul Scherrer, in Göttingen, Germany, and independently, marginally later, by an American, Albert W. Hull in Schenectady, USA. The birth of powder diffraction came four years after the discovery of the phenomenon of single-crystal diffraction made in 1912 by Walther Friedrich, Paul Knipping and Max Laue in Munich and developed from 1912/1913 by William Henry Bragg (father) and William Lawrence Bragg (son), and later by many others. Powder diffraction became a milestone towards an understanding of the nature of materials, especially of those which cannot be prepared in the form of suitable single crystals, and permitted rapid progress in solid state physics and chemistry. The events leading to the discovery of powder-diffraction phenomenon are briefly reviewed. The importance of synchrotron powder diffraction studies, which have developed since 1980s, is emphasised.

1. CONCEPTION AND INCUBATION

Discovery of X-rays and their diffraction by single crystals

For many years before the first diffraction experiments, scientists were convinced that crystals are built from regular lattices of some elementary units of matter, now called atoms. Such opinions were inspired mostly by the regular shapes of natural crystals. An important contribution was the classification of the lattices elaborated by Moritz Ludwig Frankenheim (1842) [1], a professor at the University of Breslau (Wrocław) in Silesia, and that presented in 1848 and published in 1850 by Auguste Bravais, a professor of Ecole Polytechnique in Paris, who showed that two of Frankenheim's fifteen lattices are equivalent [2]. At that time, there was no experimental way to prove that the crystals are composed from such lattices. The principal event on the way to change this situation was the announcement of the discovery of X-rays by Wilhelm Conrad Röntgen[a] [3, 4] in Würzburg, Germany on 28th December 1895. The discovery followed earlier observed but unexplained phenomena caused by so-called cathode rays in Crookes tubes. Looking for diffraction effects was a natural direction of further search. The expected diffraction was hoped to be helpful in elucidation of the nature (electromagnetic or corpuscular) of the then mysterious X-rays. The same year, Arnold Sommerfeld has completed his habilitation work on the mathematical theory of diffraction [5]. Very soon, in his third paper [6] Röntgen mentioned that his numerous experiments did not reveal any effects of diffraction by either slits nor crystals. In the period 1896-1911 some basic properties of X-rays were described such as polarisation, wavelength (its rough estimation) and presence of characteristic lines (*cf.* Table 1). Some new experiments aiming to demonstrate diffraction from slits gave results which were not fully positive, the effects being weak due to (understood later) the polychromatic nature of applied X-ray beams. In 1912, Walther Friedrich, Paul Knipping and Max Laue [7] showed the first diffraction effect by a copper sulphate single crystal (see also [8]). This breakthrough took place at about Easter 1912. The experiment was proposed by Friedrich after a discussion with Max Laue who in turn was inspired by Paul Ewald during their meeting (in January or February 1912) aiming for presentation of some conclusions of Ewald's just prepared thesis. Arnold Sommerfeld (Ewald's supervisor) discouraged making the experiment because of a conflict with Friedrich's regular occupations. After a failure of the (finally undertaken) experiment, the researchers were about to give up, but Knipping proposed then to position the film in a different way, *i.e.* behind the irradiated sample. This setting led to the first observation of diffraction by a crystal. This, and the following experiments performed for zincblende and other crystals using an improved apparatus, were a great success (announced in June 1912 and published soon after [7]), although understanding of the wavelengths involved and the lattice types was not yet complete. It is noteworthy that Röntgen, working at the same university, did not accept [9] the results obtained by the Laue's team.

Improvements came very soon. In a short time, other researchers started to publish diffraction results for the above-mentioned and other substances, as well as theoretical considerations. After some very short communications [10, 11], three key papers were published by William Lawrence Bragg (son) [12, 13] and jointly with William Henry Bragg (father) [14] in 1913.[b]

[a] On December 28th, 1895 his first paper was published entitled W.C. Röntgen, "Über eine neue Art von Strahlen" ("On a new kind of rays"), in the *Sitzungsberichte der Würzburger Physikalischen-Medicinischen Gesellschaft*. This article was immediately reprinted/translated in other journals.

[b] The first of the cited papers quite frequently has the year 1912 (the year of W.L. Bragg's lecture) ascribed in citations; it happens even in a basic book, *X-ray Diffraction Procedures* (by H.P. Klug, L.E. Alexander; Wiley 1974), where in two succeeding chapters different years are ascribed to the written form of the Cambridge lecture).

Table 1. Selected events preceding and following the discovery of powder diffraction. Underlined names: to Nobel prize winners.

Year	Achievement	Author	Institution/Town/Country	Ref.
Mar.1895	Theoretical work on diffraction	A.J.W. Sommerfeld	Univ. of Göttingen, Germany	[5]
Dec.1895	Discovery of X-rays	W.C. Röntgen	Univ. of Würzburg, Germany	
1905	Discovery of X-rays polarisation	C.G. Barkla	Univ. of Liverpool, UK	
1907	First evaluation of the X-ray wavelength on the basis of the high voltage	W. Wien	Univ. of Würzburg, Germany	
1908, 1909	Demonstration of diffraction effects on carefully prepared slits	B. Walter, R. Pohl	Hamburg, Germany	[15]
1909	Discovery of characteristic lines	C.G. Barkla	Univ. of Liverpool	
1912	Experimental and theoretical confirmation of the Walter & Pohl results (the latter provided an approximate wavelength value, $4x10^{-10}$ m)	P.P. Koch; A.J.W. Sommerfeld	Univ. of Würzburg, Germany; Univ. of Munich, Germany	[16, 17]
1912 Jan/Feb	Ewald reports to Laue the equation describing the scattering of electromagnetic waves from a lattice of resonators (included in his thesis)	P.P. Ewald (A. Sommerfeld's postgraduate student)	Univ of Munich, Germany	[18, 19 pp.40-42 & p.293]
1912 Easter to summer	Demonstration of diffraction for single crystals of $CuSO_4 \cdot 5(H_20)$, ZnS (zincblende type), PbS, NaCl, presentation of diffraction theory	Max Laue, W. Friedrich (assistant to A. Sommerfeld), P. Knipping	Univ. Munich, Germany	[20, 21]
1912	Explanation of the zincblende pattern by diffraction of white X-ray beam by the FCC crystal lattice	W.L. Bragg, W.H. Bragg	Cambridge Univ. & Univ. of Leeds, UK	
1913	Formulation of the diffraction condition ("Bragg equation")	W.L. Bragg, W.H. Bragg; G.V. Wulff; H.G.J. Moseley, C.G. Darwin	Cambridge Univ. & Univ. of Leeds, UK; Free Peoples Univ. Moscow, Russia; Univ. of Manchester & Oxford Univ., UK	[12, 14, 22, 23, 24]
1913	Ascribing atomic numbers to the elements on the basis of spectroscopic results (relation between atomic number and emitted X-rays wavelength)	H.G.J. Moseley	Univ. of Manchester & Oxford Univ., UK	[25]
1913	Visual observation of diffraction effects on a fluorescent screen	K. Terada	Tokyo, Japan	[49 p.76]
1916	Powder diffraction for LiF	P.J.W. Debye, P. Scherrer	Univ. of Göttingen, Germany	[26]
Jan.1917	Powder diffraction for Fe (presented at a conference in 1916), Al and Sl	A.W. Hull	General Electric, Schenectady NY, USA	[27, 28]
1927	Observation of electron diffraction	C.J. Davisson, L.H. Germer	Bell Telephone Labs, USA	[29]
1930	Diffraction of He atoms and H_2 molecules on surface of NaCl and LiF	I. Estermann, O. Stern	Univ. Hamburg, Germany	[30]
1934	Observation of interferences ("Kossel lines") of X-ray from lattice sources in a single crystal excited by electron beam	W. Kossel [c], V. Loeck, H. Voges	Gdańsk Univ. of Technology, Free Town of Gdańsk(Danzig)	[31]
1934	Fourier analysis of X-ray data (Patterson analysis)	L.M. Patterson	Massachusetts Institute of Technology, *USA*	[32, 33]
1936	Observation of neutron diffraction	D.P. Mitchell, P.N. Powers; H. von Halban, P. Preiswerk	Columbia Univ., USA; Univ. of Copenhagen, Denmark, (ETH, Zurich, Switzerland)	[34, 35]
1948	Beginnings of quantitative phase analysis	H.P. Klug, L.E. Alexander, E. Kummer	MRC Lab. of Molecular Biology, Cambridge, U.K.	[36]
1963	Time-of-flight neutron diffraction	B. Buras and collaborators	Warsaw Univ., Poland	[37]
1967	Full-profile structural analysis for neutron powder data	H. Rietveld	Energy Research Foundation ECN, Petten, Netherlands	[38, 39]
1977	Full-profile structural analysis for X-ray powder data	G. Malmros, J.O. Thomas	Univ. of Uppsala & Univ. of Stockholm, Sweden	[40]
from 1973	Diffraction using synchrotron radiation, e.g. for: (A) topography, (B) energy-dispersive powder diffraction (C) angle-dispersive powder diffraction	examples: *(A)* T. Tuomi et al. (1973); M. Hart (1975); (B) Buras et al. (1977), J. Bordas, J.T. Randall (1978), (C) Hastings et al. (1983)	A: Helsinki Univ. of Technology, Finland; H.H. Wills Physics Lab., UK; B: Daresbury Lab, UK; Copenhagen Univ., Denmark; C: Broohaven Natl. Lab, USA	A [41, 42]; B [43, 44]; C [45]
from 1980s	Hundreds of structures solved using diffraction data collected at synchrotrons, see sec. 6			

[c] Walther Kossel was a laureate of the Max-Planck prize (1944). His father, Albrecht Kossel, and supervisor, P.E.A. Lenard, were both Nobel laureates (in different disciplines).

It should be emphasised that the Braggs' choice of crystals studied was not accidental: first W.L. Bragg's investigations aimed to verify the structures predicted by W.J. Pope and W. Barlow on the basis of a spheres-packing model [19 *p.30*]. The verification was positive for halides but the zincblende showed a different structure than predicted.

The time of father and son from the beginning of the work on the subject to the success was quite short. Before the discovery, W.H. Bragg spent many years in Adelaide, Australia, as a lecturer of physics and mathematics at the university (his son born of an Australian mother and educated in Australia is frequently considered there as an Australian citizen). After the discovery of X-rays he installed an X-ray tube at the university, but experiments did not attract him then. At the age of 41, in 1904, he changed his interests, for the first time, from teaching towards research and started to work on radioactivity and X-rays, phenomena discovered some years earlier. These occupations continued after his return to England (to Leeds University) in 1909. He created and for a long time defended a corpuscular theory of X-rays, which at that time was supported only by few scientists. A breakthrough took place in the summer of 1912, just after the announcement of Friedrich, Knipping & Laue's successful X-ray diffraction experiment, when collaboration with his son William Lawrence started (W.L. Bragg had just graduated and became W.J. Pope's assistant at the Cavendish Laboratory, Cambridge). They used the X-ray spectrometer, invented and built by W.H. Bragg in 1913, which could be applied for both completely new X-ray fields: spectrometry and structural studies. W.H. Bragg concentrated mostly on spectrometry but also took part in solving some structures, *e.g.,* that of diamond. The father's and son's collaboration (lasting only about two years in the period 1912-1914) has resulted in the jointly awarded Nobel prize (1915) which came to them at the age of 53 and 25, respectively. However, they could not go to Sweden and receive the prize at that time due to the continuing war. W.L. Bragg remains the youngest-ever Nobel laureate.

Experimental achievements were followed by theoretical ones. Shortly after the first report, Laue presented the general mathematical diffraction conditions (Laue equations) [21]. In 1913, independent papers from three teams appeared with a simpler formulation, namely the equation describing the diffraction condition by a crystallographic plane now known as the Bragg equation: by: (i) W.L. Bragg [12] and W.L. Bragg & W.H. Bragg[d] [14] (it is noteworthy that W.L. Bragg does not mention the equation among his achievements [8]), (ii) G.V. Wulff[e] [22], and (iii) by H.G.J. Moseley and C.G. Darwin [23]. Soon, complete diffraction theories were elaborated by Ewald, Darwin and others (for details see, *e.g.*, Ref. [46]).

The discovery of the phenomenon of X-ray diffraction by crystals was made at the time of the beginnings of understanding of the atom structure. Important contributions to atomic structure were the Bohr's model of the atom and the Moseley's work in Rutherford's laboratory on the relation between the atomic number and the wavelength of emitted X-rays (both in 1913) [25]. As C.G. Darwin notes [47], Rutherford was against the X-ray experiments in his laboratory, on the ground that nobody in Manchester knew the technique of X-rays. Fortunately, Moseley did not obey. The successes he gained in a very short time, in particular the discovery of the law ($\lambda = k/(Z - \sigma)^2$), with k and σ being constants for the given spectral line) showing how the wavelength of a characteristic line depends upon the nuclear charge of the atom (it is commonly known as Moseley's law), were certainly influenced by the principles which Moseley applied in his work [47]:

Principle 1: "When one starts to set up an experiment, one must not stop for anything until it is set up,"

Principle 2: "When one starts the experiment itself, one must not stop until it is finished".

Working in this way, he also acquired the useful expertise of how to get a meal in Manchester at 3 a.m. As at that time the nature of the (still hypothetical) atom was unknown, the Moseley law gave a support to the construction of models of electronic structure of the atom by Kossel [48].

It is also worth noting that T. Terada in Tokyo was probably the first to observe strong diffraction effects on a fluorescent screen; movements of the spots were clearly visible during crystal rotation [49].

The discoveries described above have resulted in a great interest all over the world, and from that time many awards were connected with crystallography. In Table 2, selected Nobel prizes and Aminoff prizes are listed. Both kinds of prizes are presented to the laureates by His Majesty King of Sweden. Receiving one of them does not exclude the receipt of the other, as shown by the case of G.C. Shull.

In summary of this section:

Owing to the inspiration of Pope and Ewald, despite some objections from Sommerfeld and Rutherford, and rejection by Röntgen, the determination and thirst for knowledge of experimentalists Knipping, Friedrich, Braggs and Moseley, and theoreticians Laue, Darwin and Wulff (to name only a few) opened the world of ordered lattices building the single crystals to the science. This great change caould be concluded in about one year from the first experiment.

[d] The publication was preceded by a lecture for the Cambridge Physical Society in October 1912.

[e] Georgi Viktorovich Wulff (Wulf) was then a professor at the new private Free Peoples' University in Moscow; for some years until 1905 he was a professor at the Imperial (Russian) University of Warsaw, and until 1911 at the State University in Moscow. (Since 1905 the Imperial University had to exclude non-Russian professors and it was boycotted by Polish students). At the Imperial University (the only university in Warsaw, existing until 1915 in Warsaw and later, until 1917 in Rostov in south Russia), women were not admitted. Due to this restriction, Maria Skłodowska (later: Mme Curie) had to get education in France, as numerous other Polish and Russian ladies. It is noteworthy that French universities were closed until at least late 1880s inaccessible to French girl students but to foreign ones they started to be open a decade earlier.

Table 2. Selected Nobel prizes connected with crystallography, and Aminoff prizes for achievements in crystallography. NPP, NPC, NPM denote the Nobel prizes in physics, chemistry and medicine, respectively. AP stays for the Aminoff prize.

Year	Laureate(s)	Country	Prize	Achievement
1901	Wilhelm Conrad Röntgen	Germany	NPP	Extraordinary services he has rendered by the discovery of the remarkable rays subsequently named after him
1914	Max von Laue [f]	Germany	NPP	Original observation and explanation of X-ray diffraction from crystals
1915	William Henry Bragg (father), William Lawrence Bragg (son)	UK	NPP	First solving of atomic structure of crystals
1917	Charles Glover Barkla	UK	NPP	Discovery of the characteristic Röntgen radiation of the elements
1936	Peter J.W. Debye	Netherlands	NPP	Contributions to our knowledge of molecular structure through his investigations on dipole moments and on the diffraction of X-rays and electrons in gases
1954	Linus Carl Pauling [g]	USA	NPC	Understanding of the chemical bond, derived in part from crystal structures
1962	Francis Harry Compton Crick, James Dewey Watson, Maurice Hugh Frederick Wilkins	UK	NPM	Elucidation of structure of DNA from diffraction from fibres of the molecule
1962	Max Ferdinand Perutz, John Cowdery Kendrew	UK	NPC	Studies of the structures of globular proteins
1964	Dorothy Crowfoot Hodgkin	UK	NPC	The structure of vitamin B12 by X-ray crystallography
1976	William N. Lipscomb	UK	NPC	Studies on the structure of boranes illuminating problems of chemical bonding
1979	Paul Peter Ewald [h]	Germany	AP	Fundamental contribution to the development of the science of crystallography
1982	Aaron Klug	USA	NPC	Development of crystallographic electron microscopy
1982	Gunnar Hägg	Sweden	AP	Pioneering application of X-ray crystallography in inorganic chemistry
1985	André Guinier	France	AP	Fundamental experimental and theoretical studies of the dispersion of X-rays with application to the study of structures of condensed systems.
1985	Herbert A. Hauptman, Jerome Karle	USA	NPC	Development of direct methods for crystal structure determination
1988	Johann Deisenhofer, Robert Huber, Hartmut Michel	Germany	NPC	Determination of the structure of a membranebound protein
1990	Jack Dunitz	Switzerland	AP	Eminent way of using structure analysis as a tool for studying different chemical problems
1993	Clifford G. Shull	USA	AP	Development and application of neutron diffraction methods for studies of atomic and magnetic structures of solids
1994	Bertram N. Brockhouse (a), Clifford G. Shull (b)	Canada/ USA	NPP	Pioneering contributions to the development of neutron scattering techniques for studies of condensed matter: the development of neutron spectroscopy (a), the development of the neutron diffraction technique (b)
1995	Hugo M. Rietveld	Netherlands	AP	Development of profile refinement methods for the analysis of powder diffraction data
2001	Kenneth C. Holmes	Germany	AP	Pioneering development of methods to study biological macromolecules, in particular muscle proteins, by synchrotron radiation
2002	Leslie Leiserowitz Meir Lahav	Israel	AP	Fundamental studies of crystal growth and application to separation of enantiomers and for your studies of surface structures by synchrotron radiation
2005	Ho-Kwang Mao	USA	AP	Pioneering research of solid materials at ultrahigh pressures and temperatures
2006	Stephen Harrison, David Stuart	UK	AP	Remarkable contributions in virus crystallography

[f] In 1913 Max Laue's father was raised to hereditary nobility in 1913, so from that time the son's name was written as Max von Laue.
[g] Linus Carl Pauling (1901–1994) was the only winner of two unshared Nobel Prizes in different categories: the second one was the Peace Prize in 1962 awarded for his efforts to prevent the testing and use of nuclear weapons.
[h] P.P. Ewald is additionally honoured by International Union of Crystallography which awards a prize of his name at each Congress.

2. BIRTH

Discovery of diffraction of X-rays from polycrystals

The way to the elaboration of the powder diffraction (PD) method [19 *p.77*] was not straightforward. Some results of experiments performed on powders or samples having a polycrystalline component were published as early as 1913 by W. Friedrich and H.B. Keene [50, 51], but the meaning of the observed rings was not understood at that time. The first experiments on polycrystals performed by Paul Scherrer were guided by Peter Debye's suggestion that "*specific diffraction effects should be produced with X-rays by the regular spacing of electrons on circular orbits*" [52]. The initially unsuccessful experiments did not discourage Debye and Scherrer: they constructed a camera (now called a Debye-Scherrer camera) which, when joined with a source of characteristic X-rays, produced a LiF diffraction pattern with inexpectedly sharp lines. Explanation of this pattern [26] became the basis of the PD method [i]. On the other side of the Atlantic ocean, Albert W. Hull, who until 1916 had nothing in common with crystallography, but became interested, in particular, in magnetic properties of some elements, asked W.H. Bragg (after a lecture delivered during his visit in USA on X-ray diffraction from single crystals) about the structure of iron. Hearing that it had not been solved and knowing that no single crystals of iron existed, he immediately realised that when using a monochromatic source, the polycrystaline material should give all diffraction lines in a single pattern. He constructed a camera and collected data. However, the data for iron remained unsolved for some months due to a calculation error by an assistant. In the meantime, Hull solved the structures of tungsten powder and of Fe-Si single crystal, and only then started new calculations for polycrystalline iron data. The results were presented at the Cleveland Meeting of the Physical Society (27-18 Oct. 1916) and submitted to Physical Review where they appeared in January 1917 [27]. Hull's fascination for the study of the structure of iron is illustrated in his reminiscences [53]:

> *"...Immediately I became suspicious about*
> *the interpretation of my diffraction patterns, and*
> *while riding home on my bicycle at noon*
> *I made the calculations*
> *and found that the patterns agreed perfectly*
> *with a body-centered lattice".*

Hull has described the method in detail in Ref. [54]. He (partially in fruitful collaboration with Wheeler P. Davey) has solved the structure of a large number of substances, mainly elemental metals; it was he who first described the HCP metal structures. However, after a period of less than a decade he returned to his primary interests and constructed advanced magnetrons and thyratrons.

W.L. Bragg investigated mostly single crystals, but in his laboratory A.J. Bradley worked on the PD method from the early 1920s and solved a number of structures (*e.g.* α-Mn, Se, Te).

It is worth noting that the discovery of Debye and Scherrer in Göttingen could be achieved because they, as foreigners, were not affected by conscription to the army, whereas Hull could work on the method because the war started later for the USA. The war, indeed, had more influence on crystallography. The work on X-rays had to be abandoned or reduced at that time. Some X-ray scientists lost their life or were wounded. Some others, having a better chance, profited from the silence on their fronts working on the crystallographic problems there. W.H. Bragg worked on submarine detection. W.L. Bragg was at the front working on the method of detection of the enemy's batteries (the "Sound Ranging" project). The results of the latter made it possible to locate guns and determine their calibre. Lawrence Bragg's brother Robert was killed in Dardanelle. Hull worked (independently of W.H. Bragg) on submarine detection. (Both the latter task and the continuation of the Sound Ranging project, were the subjects of work of W.L. Bragg during the Second War.) Wilhelm Wien had to work on military communication [55]. *Moseley lost his life when landing in Gallipoli (ancient name: Heliopolis) on 10.8.1915 (more information on his life can be found in Refs* [56, 57]*). Aleksei Shubnikov (then a close collaborator of G.V. Wulff) was heavily injured in a battle near Warsaw in 1914, but he continued his scientific work during some periods of the war* [58]. *Ewald, sent to the (stable) northern Russian front (where he operated an X-ray diagnostic source for medical purposes* [46]*), was able to work on the dynamical diffraction theory whilst there* [59].

3. YOUTH

Development of the method before 1939

Since the discovery of single-crystal diffraction, the traditional descriptive crystallography was completed by a powerful tool permitting for understanding of the internal crystal structure. Powder diffraction extended the field of operation to all solid objects (except amorphous substances). From the second decade of 20th century, powder diffraction and single-crystal diffraction methods were used in parallel in crystal structure analysis. However, the field of operation of PD (unlike the single crystal diffraction) extends to the multiphase materials, so PD became the key method of phase analysis, leading to an understanding of the phase composition and crystal structure of many substances of high importance for physics, chemistry and technology.

Later on, diffraction studies were extended from the use of X-rays to the single crystal and powder diffraction of neutrons and electrons. He atoms and H_2 molecules were shown to diffract, also (*cf.* Table 1). The importance of neutron diffraction comes from the strong scattering of various light atoms and the ability to detect magnetic order, whereas electron diffraction extended the possibilities of PD method to very local studies.

The method advanced and, progressively, enabled the solution of structures of lower symmetries and larger cells. Experiments at non-ambient pressures and temperatures soon created new fields of investigation. All this

[i] Surprisingly, some biographies of Peter Debye tell about his various achievements but do not even mention the powder-diffraction invention among them.

happened in the first two decades after the initial discoveries. The first period of development of PD ended with the beginning of the Second World War. To demonstrate the influence of the war and the economic and political situation of the world on crystallography the ICSD database [60, 61] was analysed. The political/economic changes during (Big Crisis, second World War) are clearly visible through inflections in a graph presenting the annual variations of total number of structural datasets in (see Figure 1). Certainly, at that time there were other things to do than solving and publishing crystal structures.

Already during the first decades of diffraction, many researches have been inspired to complete their studies in physics, chemistry, mineralogy, biology, *etc.* by use of powder diffraction. Such structural studies stimulated the development of many areas of science and technology.

Nowadays, the easily available commercial diffraction instruments ensure high quality of collected data. However, in the early stages of diffraction, the equipment depended on the inventiveness of the researcher. Debye and Scherrer have built they cylindrical camera having no template for that device. The story was similar for the first flat-film X-ray camera of Hull. Linus Pauling, when needing to start studying powder diffraction experimental work, took a generator from a dentist and sculpted a camera from pieces of wood. Then, he could immediately start the measurements [62]. *He also describes an early construction of a simple pressure cell which could be applied in diffraction studies. Some data on early instrumentation may be found in Ref.* [63].

4. MATURE AGE

Progress of the method from 1945 to 2005:

Development of instrumentation at classical sources

After the Second World War, rapid progress in powder diffraction methods took place. The progress in the speed of data collection and quality of results was due to the development of instrumentation (automated diffractometers, goniometers, generators, detectors...), as well as the availability of digitised data and to numerical methods of pattern solving and refinement. Some information on instrumentation and methods of interpretation can be found *e.g.* in Refs. [64, 65]; a recent review of diffraction geometries is given in Ref. [66].

Birth and development of the Rietveld method

The idea of Hugo Rietveld to refine the whole profile of a diffraction pattern arose at early days of the era of digitised data, and led to a computational method which yields information on the crystal structure of materials which cannot be prepared in the form of single crystals [38, 39]. The method can be used to extract structural information of lesser or greater detail for the components of polyphase materials and thus it provides a foundation for quantitative analysis. Rietveld calculations can support, also, the identification of secondary phases which sometimes are difficult to analyse due to severe peak overlap. Initially, in 1967, the Rietveld method was designed for neutron PD data but a decade later it was extended to the more complex X-ray case. Presently available Rietveld software offers many options. Especially important is the opportunity to perform joint refinement from a number of experiments performed for the same sample (neutron and X-ray data, single crystal and polycrystal data).

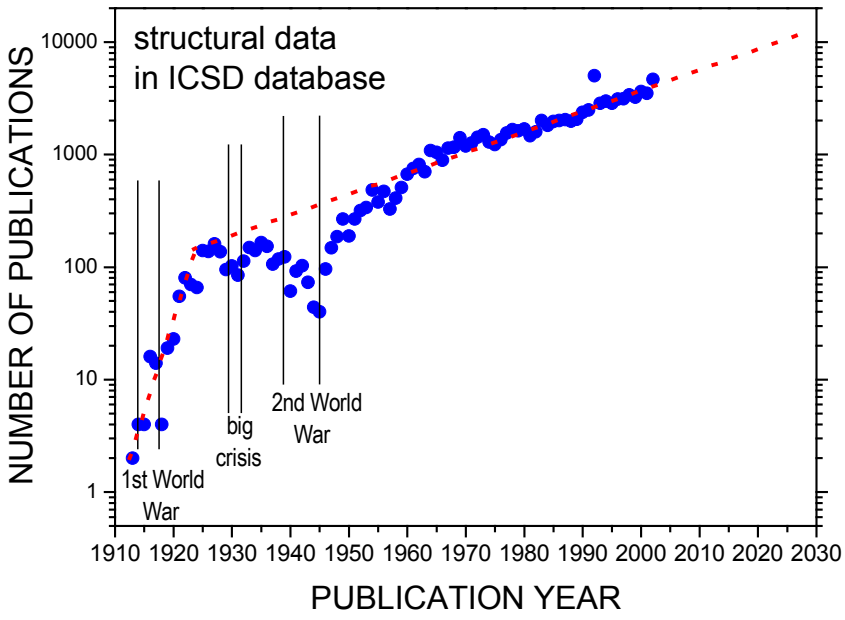

Figure 1. Inorganic structures (all entries in ICSD, see text) determined or redetermined between year 1913 and 2003 as a function of the year of publication. The reduction of published structural data due to the Big Crisis (1929-1932) and Second World War is identified. The guide-to-eye dotted line shows the basic trend observed.

Diffraction at synchrotron sources

Classical X-ray diffraction suffers from limitations connected with restricted wavelength selection and slow data collection. These difficulties are overcome by using synchrotron beams. During the 1970s dedicated synchrotron laboratories began operation and the PD results from such sources have made a significant contribution to the literature from the mid-1980s (*cf.* Figure 2 illustrating the annual variation of number of entries in ICSD database). One of the initiators of using intense beams was Bronisław Buras (a professor at Copenhagen University; until 1968 at Warsaw University and Institute of Nuclear Research in Świerk, Poland), who, with collaborators, developed the new field of energy-dispersive PD which is particularly suitable for synchrotron experiments at high pressure (earlier, he was one of the originators of the Time-of-Flight (TOF) neutron-diffraction method [37]). In the 1970s, he participated in designing of synchrotrons in Hamburg and then in Grenoble. Examples of early synchrotron PD studies are given in Table 1 (see also references in the citation given, and Ref. [67]). The dominant role of synchrotrons in high-pressure studies is reflected in the high number of corresponding entries in the ICSD database [68].

Synchrotron laboratories significantly contribute to the physics and chemistry of condensed matter, to materials science, medicine, geology *etc*. They permit time-resolved measurements, new kinds of tomography, and the solution of protein structures, and open up many other kinds of fascinating previously inaccessible domains of study. There are about 75 synchrotron and free-electron-laser light sources worldwide and the number of users amounts to 20,000 per year [69]. (For a general up-to-date information on synchrotron sources, see the proper website [70]). These modern light sources (the term of "light" is used here to describe a broad spectral range, from the infrared light to hard X-rays) provide ultrahigh beam intensity, high coherence, high collimation, and pulse duration down to the femtosecond range. They have become centres promoting international experimental projects, thus stimulating a broad international collaboration. Moreover, the advanced techniques applied at the constructed synchrotron rings and associated beamlines provide a great stimulus for the development of modern scientific and technical equipment - these techniques propagate into other domains of science and technology. For a comprehensive survey of problems specific to PD at synchrotron sources, see Ref. [71].

Diffraction studies at synchrotrons require beams with energy of at least 8-10 keV for standard purposes and much higher values for some kinds of measurements (*e.g.* at high pressure [72]). The number of beamlines dedicated to PD is thus limited. Diffraction techniques available at some specialised beams permit the investigation of samples of extremely small sizes for single crystals (studies of submicrometer-size crystals can be found in literature) and down to about five micrometers for powder samples. The latter opportunity is used, in particular, for diffraction at the highest accessible pressures (up to 300-400 GPa - *i.e.* at the conditions existing at any depth in the interior of the Earth [73]).

Sokołowski has noticed [68] the particularly large role of synchrotron structure determination for zeolites in 1990s. At present, a lot of work on protein structure is done using single crystal diffraction data, but powder diffraction methods are now starting to be useful as well [74].

From 1979 Aminoff prizes are awarded to scientists having brought an important contribution to crystallography. It is worth noting that all five Aminoff prizes awarded to eight scientists in the 21st century involved studies exploiting the synchrotron light (see Table 2).

5. SOME REMARKS ON EARLY DAYS OF DIFFRACTION IN POLAND

Despite the political and economical difficulties during the first years of independence following the establishment of peace in 1920, the importance of X-ray diffraction was soon appreciated at Polish universities. Former students of Wulff lived here (in the beginning of 1920s - shortly before his death in 1925 - they invited him for a visit to Poland, but he did not get a passport). It is interesting to put together the available data on early X-ray laboratories here. Some information was found on such laboratories at almost all universities and polytechnic schools existing at that time (see Table 3). To the best of the author's knowledge, powder diffraction was a dominating X-ray method in the laboratories listed.

Most of the laboratory leaders indicated in the Table 3 survived the Second World War (only S. Kreutz died in 1941) and, with exception of J. Czochralski and I. Feszczenko-Czopiwski,[j] after the end of the war performed the difficult task of rebuilding and equipping their ruined or requisitioned X-ray laboratories from the scratch. In 1962 Ewald noticed (see Chapter 6 in Ref. [19]: "*In Poland there are X-ray laboratories at the six universities and some more at state or academy institutions, but the output seems not to be high.*" Nevertheless, the crystallography in Poland developed steadily, although results were not always published in international journals. Such early work from the Warsaw academic centres includes, *e.g.* studies on the structure of fossil rubbers [75] (here, the results for unusually small samples could be performed at an ordinary Debye-Scherrer camera due to ingenious mounting the grain to the collimator tip [76]), pigment identification [77], and studies of coals and graphites [78, 79], performed in Warsaw University in mid-1950s, and the solution of the β-boron structure (which had remained unsolved for forty years since Scherrer's unsuccessful efforts [80]) at the Institute

[j] The former subjected to unjustified accusations could not return to science, the latter had an "improper past" (he had been a deputy-premier in independent Ukrainian government about 1919-1920), so he was arrested in Poland in 1945 by Soviet security services and condemned for 10 years of Gulag camp in Siberia where he finally died on 2nd Sept. 1952. The absence of both these eminent scientists was a great loss for the Polish academic community as well as for the metallurgical industry.

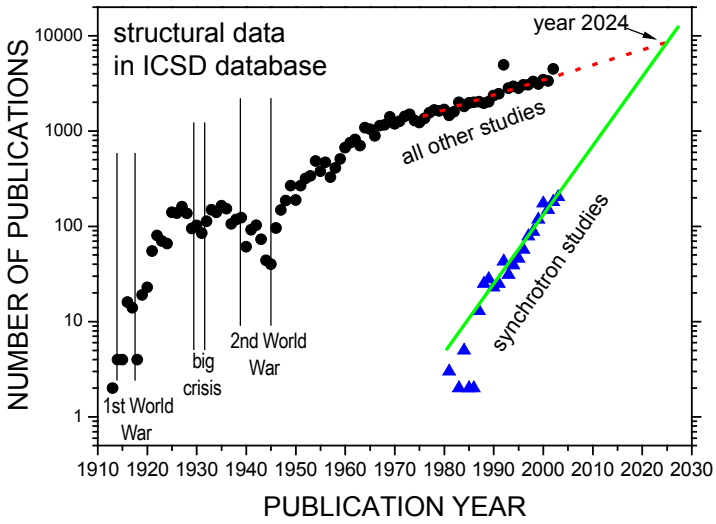

Figure 2. Inorganic structures (entries in ICSD, see text) determined or redetermined between year 1913 and 2003 as a function of the year of publication. The numbers of structural data represent the results in the database obtained for non-synchrotron data (circles) and for synchrotron-based data (triangles). Both, powder and single crystal reports are included. The reduction of structural data due to the Big Crisis (1929-1932) and Second World War are identified. Several papers from the 1950s and 1960s, erroneously classified in the ICSD database as synchrotron studies, are eliminated.

of Physics PAS [81]. (The authors of the studies mentioned originated from the post-war laboratories of S. Pieńkowski and L. Chrobak who continued their earlier activity.) In 1956 the first meeting of Polish crystallographers was organised by W. Trzebiatowski. These local meetings are held each year in Wrocław from then onward. Moreover, conferences on applied crystallography take place, typically in Wisła, every third year, and Poland has hosted one world crystallographic congress (Warsaw 1978) and two European meetings (Wrocław 1986, Cracow 2001), and will host the European Powder Diffraction Conference, EPDIC, in 2008.. Many smaller related schools and conferences such as the ISSRNS International Symposia have been organised by local scientific institutions. In 1975 there were eighty eight X-ray diffractometers and one neutron diffractometer in scientific institutions in Poland [82]. Now, numerous modern diffractometers are employed at all large universities, and numerous scientists perform diffraction experiments at various large facilities in the world each year (the first version of a database of synchrotron-related Polish publications exceeds one thousand entries [83]).

Table 3. X-ray laboratories at four Polish universities and three polytechnic schools in 1920s and 1930s.

Town	Faculty & University	Laboratory head and collaborators	Probable start of activity	Field	Additional information
Warsaw	Fac. of Physics, Warsaw University	Prof. Stefan Pieńkowski	1920s	physics, crystallography	[84]
Poznań	Fac. of Agriculture and Forestry, Poznań University	Prof. Stanisław Glixelli (*) Dr. Aleksander Nowakowski Kazimierz Boratyński,	1920s	chemistry	[85]
Lwów	Fac. of Chemistry, Jan Kazimierz University	Prof. Ludwik Chrobak, Prof. Włodzimierz Trzebiatowski (from 1938), Józef Chojnacki	~1929	chemistry, crystallography	[86]
Cracow	Dept. of Mineralogy & Crystallography, Jagellonian University	Prof. Stefan Kreutz (**)	~1930	mineralogy	[86]
Poznań	Fac. of Chemistry, Poznań University	Prof. Alfons Krause, Dr. Anzelm Lewandowski	~1930	chemistry	[87]
Warsaw	Inst. of Metallurgy, Warsaw University of Technology	Prof. Jan Czochralski Michał Śmiałowski	X-ray equipment: ~1930s	metallurgy	[86]
Lwów	Dept. of Physical Chemistry, Lwów Polytechnic School	Dr. Włodzimierz Trzebiatowski W. Bryjak	1930s	chemistry	[86]
Cracow	Fac. of Metallurgy, AGH University of Technology	Prof. Władysław Łoskiewicz ,Prof. Iwan Feszczenko-Czopiwski (***) Dr. Zygmunt Jasiewicz	1930/1934	metallurgy	[86, 88]

(*) Former student of G.V. Wulff.
(**) The author of a book on crystallography written together with a mathematician S. Zaremba [[a]].
(***) Head of the laboratory in 1920s before installation of the modern X-ray equipment, in 1930s engaged mainly in industry.

6. APPLICATIONS AND FUTURE TRENDS

The power of synchrotron light

From its beginning, powder diffraction became an important field of crystallography and played a part in the progress of physics, chemistry and mineralogy, for which an understanding of atomic structure is essential. Various aspects of this progress can be found as seen at the earlier stage (see Ref. [89]) and at earlier stages in Refs. [90, 91] as well as in many others. It is not possible to enumerate all recent achievements of the PD method in the analysis of structure, phase analysis, elastic properties, size and strain studies or texture analysis. Only some selected illustrative examples can be given here. PD is used in modelling the mineral phases forming the interiors of the Earth and other planets, in forensic investigations [92], in phase analysis of rocks from the moon and even in phase identification of interplanetary dust [93, 94]. The list of applications is long (for some others see, *e.g.* Refs. [65,91])**.**

At present time, PD is evolving in several directions - some of which could not have been imagined at the beginning of the development of the method. Modern X-ray sources and beam conditioning devices permit the optimal selection of experimental conditions. There is a wide variety of available beams, which differ in flux, collimation, divergence, degree of monochromaticity and wavelength tunability. The available ranges of these parameters at classical and synchrotron sources provide the conditions for the studying of diverse kinds of samples: thin/very thin layers, irregularly shaped and minor size samples or extremely large objects.

Narrow beams can be useful for studies of single crystals as well as polycrystals. The size of the required single crystal sample decreases in correspondence with improvements of beam focusing and collimation optics. Moreover, it has become possible to scan a polycrystalline sample with a narrow beam of micrometre section. Therefore more detailed (not integrated) information is obtained on the crystallite orientation and distribution. Intense nanobeams (down to tens of nanometres) are becoming available also, and they will create new fields of exploration. In powder diffraction investigations, the key advantages of using synchrotrons are: the possibility of time-resolved studies, the opportunity to select the wavelength, the ability to perform diffraction on tiny samples, and the availability of data with high-resolution and high statistics.

It is also worth noting that the powder diffractometers used for PD can be used, with or without some small modification of the optics, for a broader class of purposes, such as reflectometry, porosity imaging [95], characterisation of nanostructures and disordered structures [96, 97]. The latter is particularly important, as nanopowders become a quickly developing field of study. Thin polycrystalline layers can be studied by diffraction (yielding the phase composition) using flat sample diffraction geometry as well as by reflectometry at low angles (at, possibly, the same instrument) with output information concerning the stacking details, thickness, density and surface/interface roughness.

A recent worth mentioning example concerns the depth profiling being a task of interest for technology and industry. The technique of spatially resolved energy dispersive X-ray diffraction is demonstrated to permit depth profiling up to a depth of 4 mm in cement samples if a suitable high-energy synchrotron beam is used [98].

The number of solved and refined structures is a good index of progress in crystallography. This number grows each year and its growth shows the importance of crystallography in solving problems in physics, chemistry, mineralogy and technology. Of course, the importance of PD methods is not identical in those four domains and varies with time. Figure 2 compares the amount of data collected with synchrotron and remaining sources (both, single crystal and powder techniques applied). The extrapolated lines meet at the date of 2024 meaning that the prognosis is that about the year 2024 the synchrotrons will provide competitive number of datasets.

Figure 3 illustrates the difference in the growth rate of data collected with different ways. The three different slopes show that the contribution of powder diffraction data to the body of structural knowledge slowly but systematically increases with time, whereas the contribution of synchrotron powder diffraction data increases dramatically.

Figure 4 refers to powder diffraction data: it presents the fraction of inorganic structures solved/resolved/refined by PD with synchrotron data. If the trend continues, 50% of structures will be solved with synchrotron data in about 2025 (the use of a logarithmic scale suggests an even earlier date of year ~2017 (see Figure 3). It seems certain that in two decades from now, synchrotron data will dominate in structure determination. Two factors are involved here: i) the growing access to PD beamlines and possible future development of remote control systems, ii) the excellent resolution and data statistics which make it possible to solve structures which were previously unsolvable (multicomponent phases, large cells, low symmetries). One of recent achievements is the protein structure solved using synchrotron PD data (see, *e.g.* Ref. [74]). For the particular case of PD studies at high-pressure, the future is especially bright, as indicated by the increase in the number of beamlines being under construction, and the improvement of their parameters [99].

When searching for the phrase "powder diffraction" in the world wide web, one finds that due to typing error the letter "d" is sometimes missing transforming the result into "power diffraction" (see the examples at [100]*). This error unintentionally emphasises the true power of the method which makes it possible to understand the structure and basic properties of any crystalline material. In ten years from now, we will celebrate the* 100^{th} *anniversary of powder-diffraction power!*

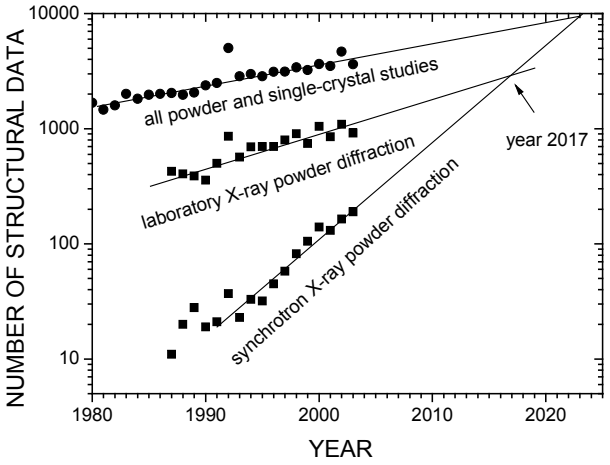

Figure 3. Trends in inorganic structures (solved or refined) according to the ICSD database.

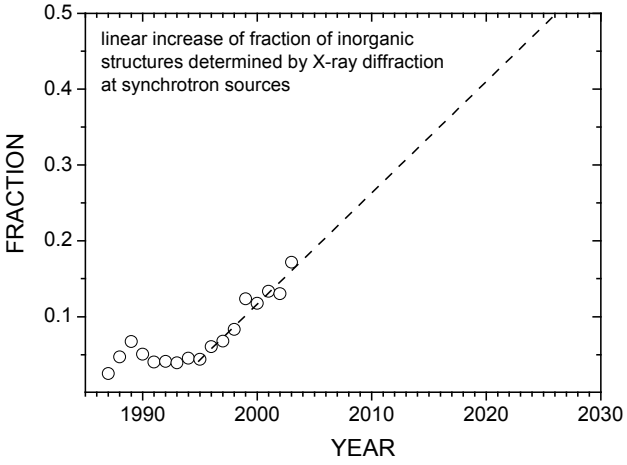

Figure 4. The fraction of inorganic structures solved/resolved/refined by powder diffraction with synchrotron data.

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