

A Century of Powder Diffraction: a Brief History

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Abstract. Almost a century has passed since the pioneering work of *Debye*, *Scherrer*, and *Hull* and their first powder X-ray diffraction experiments in 1916/17. Although these pioneers and many others discovered most of the fundamental concepts in the field of powder diffraction within the first few years, nobody at that time could foresee the development of the computer and its calculating power in the 21st century. The general availability of computing power changed the field of powder diffraction, as *Hugo Rietveld* showed with his computer-assisted whole powder pattern fitting concept around fifty years after

the first powder diffraction patterns were observed. Nowadays, much more complex algorithms are used to solve and identify crystal structures from powders. The intention of this historical review is to show some of the most important developments from the viewpoint of the authors in the field of powder diffraction in the last century, from the beginnings of the first transmission experiments and the determination of simple cubic crystal structures to the techniques of today allowing for the refinement of thousands of atoms within one unit cell.

Introduction

The twentieth century is often regarded as the century of information technology. During this time the fundamental physical, chemical, and technological concepts, which led to the development of computers and therefore to the underlying devices for information technology, were laid down. From a certain viewpoint, it can also be called the century of diffraction as the International Union of Crystallography (IUCr) lists 21 Nobel prizes on their homepage,^[1] more or less directly connected with crystallography and diffraction, in the time span between the “big bang” of experimental X-ray crystallography in 1912 and 2000. (In total there are 29 Nobel prizes listed (current status 2014), including the Nobel prize for the “Discovery of X-rays” by Wilhelm *Conrad Röntgen** [*Born March 27, 1845 in Lennep/Remscheid (Germany), died February 10, 1923 in Munich (Germany)] in 1901 and 7 additional Nobel prizes, which were awarded in the field of crystallography and diffraction between 2000 and 2014). The importance of crystallography and diffraction was also recognized by the United Nations, which announced the year 2014 as the “International year of crystallography”.^[2,3] The year 2014 also marks the 100th anniversary of awarding the Nobel prize to *Max von Laue** [*Born October 9, 1879 in Pfaffendorf/Koblenz (Germany), died April 24, 1960 in West-Berlin (Germany)] for the discovery of “Diffraction of X-rays by crystals”, which can be regarded as one of the key experiments for both experimental crystallography and diffraction. Of course

this discovery was only one of the milestones, which had to be passed before we could use diffraction as a daily tool in our research work, either in form of single crystal diffraction or powder diffraction, either in our laboratory environment or at large-scale research facilities such as synchrotrons and/or neutron sources. Since the discovery of “Diffraction of X-rays by crystals” a century has already passed and many of reviews and history books about crystallography and diffraction have been written, for example *Paul Peter Ewald*’s “Fifty Years of X-ray Diffraction”,^[4] *José Lima-de-Faria*’s “Historical Atlas of Crystallography”,^[5] *André Authier*’s “Early Days of X-ray Crystallography”,^[6] and the publications of *Paszkwic*,^[7] *Ilyushin* and *Kovalchuk*,^[8] *Cheetham*,^[9] and *Will*^[10] to name just a few. Common to all of these publications is that they give a general historical overview of X-ray diffraction and crystallography of the first half of the twentieth century, whereas the development after that time is sparsely considered. Therefore, we will attempt to give a short overview of a particular field of diffraction, namely powder diffraction, from the beginning with the first powder diffraction experiment to the current state-of-the-art powder experiments, which are nowadays supported by extensive software packages and manifold technological possibilities.

Towards the First Powder Diffraction Experiment

Over the previous centuries many people have contributed to the scientific methods, which we nowadays use in single crystal and powder diffraction experiments. Among these pioneers was *Francesco Maria Grimaldi** [*Born April 2, 1618 in Bologna (Italy), died December 28, 1663 in Bologna (Italy)], who coined the term “diffraction” when he investigated the

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behavior of light by describing the shape of the light cone after the light passed through a pinhole.^[11] A few centuries later, after many eminent scientists had elucidated the true nature of light in increasingly great detail, *Wilhelm Conrad Röntgen* made the discovery of his “X-rays” in 1895,^[12,4,6] while he was experimenting with discharge tubes, which were a hot topic of research at that time. Soon after that, in 1912, *Max von Laue*, *Walter Friedrich** [*Born December 25, 1883 in Salbke (Germany), died October 16, 1968 in East-Berlin (Germany)] and *Paul Knipping** [*Born May 20, 1883 in Neuwied am Rhein (Germany), died October 26, 1935 in Darmstadt (Germany)] conducted their famous X-ray diffraction experiment,^[13] in which they proved for the first time two fundamental principles in physics: that a single crystal is composed of regular blocks and that X-rays are waves with a wavelength in the order of the distances between the building blocks of the crystal^[4,6] (see Figure 1a). In fact, *Friedrich* and *Knipping* also carried out the first recorded powder diffraction experiment, as they ground a copper sulfate crystal and placed the powder, contained in a paper box, into the beam instead of a single crystal.^[13,4,6] Unfortunately, at this time, it seemed that the exposure time was too short and the tube quality was too low to see diffraction rings. They only saw small speckles around the primary beam spot from the very rough ground powder (see Figure 1b) and no diffraction rings from the fine ground powder.^[13,4] Nevertheless, “Diffraction of X-rays by crystals” was a huge issue and the interest of physicists all over the world was awakened. In the same year after the discovery of *Friedrich*, *Knipping*, and *von Laue*, *William Lawrence Bragg** [*Born March 31, 1890 in Adelaide (Australia), died July 1, 1971 in Walsingham/Ipswich (England)] wrote down his famous equation for the first time.^[14,4] Later this equation, besides many other discoveries, led to the award of the Nobel

prize in 1915 to him and his father *William Henry Bragg** [*Born July 2, 1862 in Wigton/Cumberland (England), died March 10, 1942 in London (England)] “for their services in the analysis of crystal structure by means of X-rays”.

Regarding powder diffraction experiments, nine months after their first publication in 1912, *Friedrich* carried out another “powder” experiment in 1913 with white sticky wax (which is in fact a polycrystalline material like beeswax^[15]), where he saw for the first time diffraction rings around the primary beam spot.^[16] The picture of this experiment and the original quote of *Friedrich* in German can be found in Figure 2. In his publication *Friedrich* was already aware that his observations must originate from diffraction (“*Diese allgemeine Verbreiterung möchte ich ebensosehr als Beugungerscheinung ansprechen wie die mehr in die Augen springenden Ringe*”) and he gave the correct explanation, that if the particles in an amorphous compound are not too small and if they are randomly distributed, one should see diffraction rings (at that time, *Friedrich* did not know that the samples he investigated, such as beeswax, are crystalline rather than amorphous). In particular he wrote (as a second possible explanation) that the single interference spots of individually distributed crystals can be summed up to an accumulation with rotational symmetry, which are in fact the observed diffraction rings. Unfortunately, at this time, he was not aware of the true nature of the size and properties of atoms and molecules as well as of the radiation, he used. In particular, he used polychromatic X-rays, which hindered a better explanation of the observations he made, especially when he changed the tube from a nickel anticathode tube to an iron anticathode tube and the position of the rings changed, whereas the diffraction spots in single crystal experiments did not change upon tube replacement.

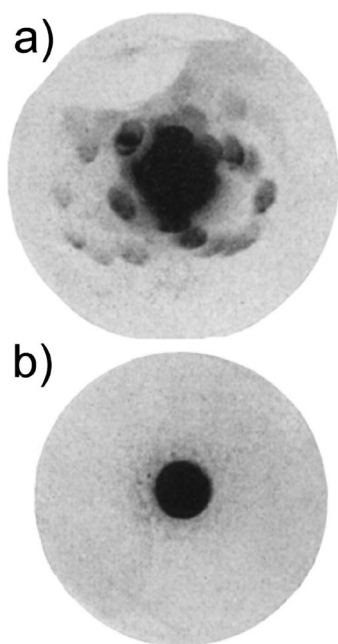


Figure 1. (a) First X-ray diffraction pattern of a copper sulfate single crystal recorded by *Friedrich* and *Knipping*.^[13] (b) Subsequent X-ray diffraction pattern of a rough ground copper sulfate crystal.^[13]

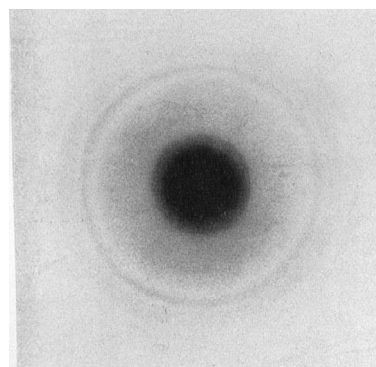


Figure 2. *Friedrich's* first “powder” diffraction rings from white sticky wax.^[16] This is a part of his original writing from his publication in 1913: “*Es wurde zunächst gewöhnliches weißes Klebwachs untersucht, das zu einem 3 mm dicken Scheibchen geformt war, und das die Strahlen senkrecht durchsetzen. Nach einer Exposition von 2000 Milli-ampere-minuten mit einer mittelweichen Röhre ergab sich auf der photographischen Platte das in Figure 1 auf Tafel XII reproduzierte Bild), auf dem man deutlich einige Beugungsringe um den Durchstoßpunkt der Primärstrahlen erkennen kann. Bei anderen Körpern, wie Kanadabalsam, Paraffin, Paraffinöl, Bernstein und Meerschaum, wurden teils ebenfalls Andeutungen von Ringen, stets aber ein viel allmählicher Abfall der Schwärzung festgestellt, als er ohne eine dieser Substanzen sich zeigte. Diese allgemeine Verbreiterung möchte ich ebensosehr als Beugungerscheinung ansprechen wie die mehr in die Augen springenden Ringe.*”.

Shortly afterwards, *Shōji Nishikawa** [*Born December 5, 1884 in Hachiōji (Japan), died January 5, 1952] and *S. Ono* carried out experiments with fibrous, lamellar, and granular substances.^[17] Like *Friedrich*, they also used polychromatic X-rays, but when they investigated granular substances like marble and fine powders of rock-salt, quartz, and carborundum, they noticed two remarkable facts. In particular, that the detached spots, which were seen before for granular substances are blended into a continuous ring, if the powder is made sufficiently fine and that the distance between the center of the primary beam spot and the maximum intensity of the ring does not change with the particle size for a given substance. Interestingly, for carborundum they observed two distinguishable rings, whereas they observed more rings for candle wax than *Friedrich* observed for the sticky wax. Unfortunately, *Nishikawa* and *Ono* did not present any pictures of the diffraction rings in their publication,^[17] but here is the original quote of them concerning their experiments with granular substances:

“Among the granular substances investigated, marble may be considered typical. The central spot is surrounded by innumerable small spots, of which the intensity is maximum at a certain distance from the centre. Somewhat similar figures were obtained with fine powders of rock-salt, quartz, carborundum, etc. The position of the maximum intensity varies with the substance, but is apparently independent of the size of grains. When the powder is made sufficiently fine, the detached spots are blended into a continuous ring, of which the radius corresponds to the distance of the maximum intensity and depends on the nature not only of the substance, but probably also of the rays. With carborundum, two conspicuous rings were obtained. It will be remarked that the ring becomes ultimately very faint when the powder is made more and more minute. Also, silica precipitated from its hydroxide shows no ring. Similar rings obtained by Friedrich with wax seems to be analogous to the above examples, though these rings are more numerous and very sharply defined than in the above examples, as was also the case in one of our photographs obtained with ordinary candle wax. It is highly desirable in these respects, to experiment with different sources of rays, using various kinds of anticathodes.”

Nowadays we know that the investigation of powders with polychromatic X-ray radiation gives, if the experimental setup is not precisely aligned, only blurred halos/diffraction rings and that the shift of the diffraction rings, which *Friedrich* saw by using different tubes originates not from the differences in the cut-off energy of the Bremsstrahlung spectrum but mainly from the changes of the characteristic X-rays. Nevertheless the description and the attempted explanations of the diffraction experiments of *Friedrich*, *Nishikawa* and *Ono* showed that there were still many things unknown about polycrystalline materials and that the explanations of *Laue* and *Bragg* were not sufficient to describe the phenomena apart from single crystals.

The Powder Diffraction Experiments of *Debye*, *Scherrer*, and *Hull*

The discovery of *Peter Debye** [*Born March 24, 1884 in Maastricht (Netherlands), died November 2, 1966 in Ithaca/

New York (United States)] and *Paul Scherrer** [*Born February 3, 1890 in St. Gallen (Switzerland), died September 25, 1969 in Zurich (Switzerland)] in 1916^[18] is a typical discovery where researchers looked for a theory-predicted phenomenon and in the process of carrying out the experiment they found another phenomenon to occur. Originally, they searched for “specific diffraction effects which should be produced by X-rays by the regular spacing of electrons on circular orbits”,^[4] but what they found when they investigated fine lithium fluoride powder, were diffraction rings originating from the “randomly oriented microcrystals of the powder” (see Figure 3). But why were they able to give that effect the right interpretation immediately? In contrast to *Friedrich* and *Nishikawa*, they were at that time fully aware of the spectrum of their X-ray source, namely, that the X-ray tube produces a bunch of characteristic X-rays. In addition, they realized that the observed sharpness of the measured intensities could not be attributed to the effect which they were looking for. Consecutive considerations led them to explanations nowadays known to every crystallographer. This includes not only the observation that the equations of von *Laue* and *Bragg* can be directly applied to powders, but also that one has to think about multiplicities, as different *hkl* planes can contribute to the same observed reflection, since the lengths of the d-vectors are identical. With the knowledge of the wavelengths of the two strongest characteristic X-ray lines, they were able to deconvolute the different intensities and they determined the lattice parameters of lithium fluoride and silicon to a very good extent.

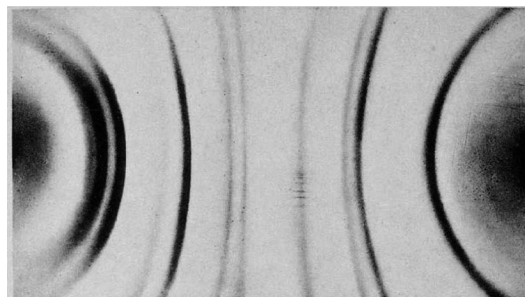


Figure 3. Diffraction pattern of lithium fluoride (LiF) with a copper anti-cathode which was shown by *Debye* and *Scherrer* in their publication in 1916^[18] (Scanned image from http://www.scs.illinois.edu/xray_exhibit/ImagePages/debyescherrerImage2.php). LiF was pressed into a rod of 2 mm in diameter and 10 mm in length.

Apparently at the same time, *Albert Wallace Hull** [*Born April 19, 1880 in Southington/Connecticut (United States), died January 22, 1966] was working at the General Electric Research Laboratory in the United States, where at the beginning he was engaged in with the investigation of his newly developed Dynatron vacuum tube with negative resistance. With reference to his autobiography,^[4] one day *Sir William Bragg* visited the laboratory and they discussed the problem why the crystal structure of iron was still not known at that time. This discussion was the origin of *Hull's* interest into the field of crystallography and X-ray diffraction. In his autobiography he wrote:

“From the start I had planned to use powder for my X-ray crystal analysis, since it was common knowledge that single crystals of iron had not been produced. I visualized that all the Bragg reflections would be recorded simultaneously, and might be unscrambled.”

As he was still quite busy with the Dynatron project when he started with first diffraction experiments, he forwarded the first iron powder pattern to an assistant, who was tasked with checking if the d-spacings of the powder patterns of iron were comparable to Bragg values for the three cubic crystal systems. Unfortunately, this assistant failed and it took some time until he could convince himself that iron has a body-centered lattice. After this success he worked out his theory of powder crystal analysis and published it in 1917, together with the first experimental results from a variety of different materials (see Figure 4).^[19] In 1919, he published another paper, in which he showed to the chemists' community that his powder diffraction analysis can be used as a fingerprint for chemical compounds even if they are mixtures.^[20]

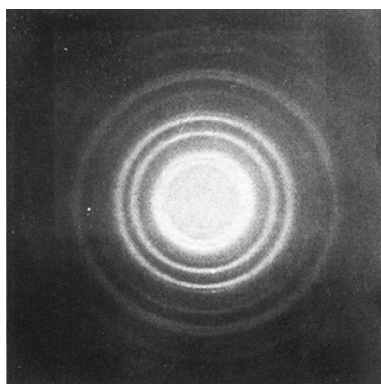


Figure 4. Diffraction pattern of aluminum, recorded by Hull in 1917.^[19] In the article he describes the picture as follows: “Figure I, Plate I, shows the pattern given by aluminium when illuminated by a small circular beam of nearly monochromatic rays from a molybdenum tube. The exposure time was nine hours, with 37 milliamperes at 30,000 volts, and crystal powder 15 cm from the target and 5.9 cm from the photographic plate. The faintness of the vertical portions of the circles is due to the cylindrical form in which the powder was mounted, causing greater absorption of rays scattered in the vertical plane.”.

In his autobiography he also wrote, that during the war it was very complicated to get foreign scientific journals and that after the war he was very surprised that one year before him Debye and Scherrer published the same method and almost the same explanations, which he found. However, if we carefully study the publications which were made on both sides of the ocean, we will find some interesting differences in the experimental techniques. For instance, Hull was using molybdenum radiation, which was first passing through a zirconium filter before hitting the sample. This zirconium filter was also the first monochromator as it suppressed most of the Bremsstrahlung background and other characteristic X-ray lines except the K_{α} lines. This made the interpretation of the obtained photographs much easier as no characteristic-line dependent calculation was needed. Additionally, Hull was the first person to carry out in situ powder diffraction experiments, as he mea-

sured an iron sample at liquid air temperature, at room temperature and at 1273 K.^[19] Unfortunately, he did not give any description of the experimental setup for his temperature-dependent measurements.

Although the general geometry of a powder diffraction experiment in transmission mode has not changed since the days when Debye, Scherrer, and Hull performed their first powder diffraction experiments, much progress with respect to instrumentation and analysis has been achieved over the last century.

In the following, we try to give in chronological order an overview of the outstanding improvements, which were made in the field of instrumentation as well as in the field of data analysis of powder patterns. We have to apologize to all those great scientists and researchers whom we could not mention here or whom we simply overlooked during our search for historic articles. In order to keep a readable scope of this article, we intend to focus on developments, which were made in the field of powder diffraction and neglect developments from which both fields, powder diffraction and single crystal diffraction, benefited.

The First 50 Years

During the first six decades after the breakthrough of Debye, Scherrer, and Hull, the crystal structures of many elements, metals, and minerals were solved and described. However, most of the crystal structures, which were solved from powder diffraction data, possess a very simple crystal structure with mainly cubic or hexagonal lattices [e.g. crystal structures of 2H-graphite (hexagonal closest packed modification, space group $P6_3/mmc$, Hull^[19] confirmed by J. D. Bernal^[21]) and 3R-graphite (trigonal space group $R\bar{3}m$, Debye/Scherrer^[22])]. Although a lot of interesting work was published during that time, we want to focus on a few selected topics to give a general overview of the progress which was made before the introduction of the Rietveld method.

(a) The Determination of the First Crystal Structures of Gases

Shortly after the discoveries of Debye, Scherrer, and Hull, the first investigations of gases in their solid state were performed. At that time condensed gases were used, which normally do not grow as sufficiently large single crystals and therefore the only way to analyze the crystal structure was to make use of the newly developed powder diffraction method. To the best of our knowledge, the first crystal structure description of a solidified gas was given in 1923, when Franz Eugen Simon* [*Born July 2, 1893 in Berlin (Germany), died October 31, 1956 in Oxford (England)] and Clara von Simson* [*Born October 4, 1897 in Rom (Italy), died January 26, 1983 in Berlin (Germany)] reported in a short note (“Zuschriften und Vorläufige Mitteilungen” in “Naturwissenschaften”)^[23] that they had investigated the crystal structure of argon (Ar) with the Debye-Scherrer method. Shortly thereafter, they published the cubic crystal structure of hydrogen chloride (HCl) (stable between 98–162 K) and the first investigations of the

low-temperature phase (stable below 98 K),^[24] followed by a longer publication of the crystal structure of argon,^[25] both in “Zeitschrift für Physik”. Almost at the same time, *Joseph de Smedt** [*Born October 20, 1888 in Sint-Niklaas (Belgium), died December 10, 1969 in Sint-Niklaas (Belgium)] and *Willem Hendrik Keesom** [*Born June 21, 1876 on Texel (Netherlands), died March 24, 1956 in Oegstgeest (Netherlands)] reported the crystal structures of carbon dioxide (CO₂) and nitrous oxide (N₂O) in 1924 in the Proceedings of the Royal Netherlands Academy of Arts and Sciences (“Koninklijke Nederlandse Akademie van Wetenschappen”).^[26] In this context, the publications of *H. Mark* and *E. Pohland*^[27,28] as well as another publication by *J. de Smedt* and *W. H. Keesom* also have to be mentioned.^[29] In 1927, *John Cunningham McLennan** [*Born October 14, 1867, died October 9, 1935] and *J. O. Wilhelm* reported a body-centered orthorhombic crystal structure for the low-temperature phase of solid oxygen^[30] at a temperature of 21 K (boiling point of liquid hydrogen). Unfortunately, this crystal structure description was not correct as we know today: the low-temperature phase of oxygen actually consists of two phases (α -phase and β -phase) and the α -phase, measured by *McLennan* and *Wilhelm*, is in fact monoclinic with space group *C2/m*.

Two years after the first experimental report of the crystal structure of solid oxygen, *Lars Vegard** [*Born February 3, 1880 in Vegårshei (Norway), died December 21, 1963 in Oslo (Norway)] submitted four short communications to “Nature” and to “Naturwissenschaften” regarding the crystal structure of nitrogen below 35.5 K. In his first communication to “Naturwissenschaften” he stated that they obtained powder patterns of solid nitrogen, which can be described by a cubic unit cell with an edge length of 11.3 Å.^[31] In the second communication to “Nature” a little later, he wrote that the cubic unit cell length is 5.65 Å^[32] and in the third communication in “Naturwissenschaften”, he gave an explanation as to why they mistakenly had chosen the wrong unit cell length.^[33] In his third communication he also gave the structural description in space group *T4* ($\equiv P2_13$), which can also be found in the fourth communication in “Nature”.^[34] An article of full length containing experimental and crystallographic descriptions was submitted to “Zeitschrift für Physik” one month later.^[35] In Figure 5, the first powder diffraction pattern of α -nitrogen from this article can be seen. The determination of space group *P2₁3* by Vegard was the start of a long-lasting debate as to whether space group *P2₁3* or space group *Pa $\bar{3}$* is the correct choice for the α -phase of solid nitrogen (these days most authors prefer space group *Pa $\bar{3}$* , although some authors are still using space group *P2₁3* in their studies). One year after the publication of the crystal structure of solid α -nitrogen, *Vegard* published the structure of solid α -carbon monoxide (CO) in space group *P2₁3* in 1930.^[36]



Figure 5. Debye-Scherrer diffraction pattern of solid α -nitrogen at the boiling point of liquid hydrogen (21 K), recorded by *Vegard* in 1929 with an iron anti-cathode.^[35]

(b) Development of Diffraction Geometries and Powder Diffractometers

In his first experiments, Hull used simple transmission geometries with a rotating thin-walled glass tube and a flat photographic plate in order to collect his powder diffraction rings.^[19] The transmission geometry was also used by *Debye* and *Scherrer*, however, in their first experiment where the sample was placed in the middle of the geometry and a photographic film was wrapped around the diffraction center.^[18] This kind of transmission geometry, today mostly known as Debye-Scherrer geometry, is still state-of-the-art if we look at modern powder diffractometers, which now use position sensitive detectors instead of films for the detection of scattered X-rays.

One of the first focusing geometries was published in 1919 by *Hugo Seemann*^[37]* [*Born April 13, 1884 in Celle/Hannover (Germany), died 1974] and in 1920 by *Helge Bohlin*.^[38] They found that if the sample is located along the focusing circle (defined by the focusing points of the X-rays which lie on the focusing circle), they can obtain much sharper diffraction rings. In this special reflection geometry, later called Seemann-Bohlin geometry, the X-ray source and the sample have fixed positions.^[39]

Around the same time, *Johannes Christian Michael Brentano** [*Born June 27, 1888 in Vienna (Austria), died 1969 in Zurich (Switzerland)] worked on the geometry, which nowadays we know as the Bragg-Brentano geometry.^[40–43] In this geometry the distance between the tube focus and the sample is equal to the distance between sample and detector slit.^[39,44] This determines that the diameter of the focusing circle is dependent on the chosen incidence angle.

In 1931, *H. H. Johann* published in “Zeitschrift für Physik” an article in which he described his new type of monochromator using a cylindrically bent crystal.^[45] Although its focusing was not yet perfect, *Johann* showed that with only a short integration time he could produce very sharp lines. Two years later, *Tryggve Johansson* improved the *Johann* monochromator, when he showed that a specially bent and cut crystal leads to a much better focusing.^[46,47]

In 1937, the focusing monochromator of *Johansson* was already used by *André Guinier** [*Born August 1, 1911 in Nancy (France), died July 3, 2000 in Paris (France)] who integrated this monochromator in his (later be called) Guinier camera,^[48,49] which has a similar geometry as the Seemann-Bohlin setup.^[44] The difference between these two methods is that the Guinier camera works in transmission mode, as the sample on the focusing circle is irradiated from an incident beam outside of the focusing circle.^[44] A modification of the Guinier camera was given by *Pieter Maarten de Wolff** [*Born July 23, 1919 in Bandung/West-Java (Indonesia), died April 10, 1998 in Delft (Netherlands)] in 1948, which allowed the measurement of different samples at the same time.^[50] With this high-resolution Guinier-de Wolff camera, *P. M. de Wolff* and *L. Walter-Lévy* solved as early as 1953 the complicated triclinic crystal structure of Korshunovskit (Mg₂(OH)₃(Cl,Br)·4H₂O) from powder diffraction data.^[51]

In 1949, *William Parrish** [*Born 1915 in Philadelphia (United States), died March 18, 1991 in San Jose/California

(United States)] published an article about the construction of an X-ray powder diffractometer,^[52] which he had previously patented.^[53–55] The development of this commercial powder diffractometer was a breakthrough^[56] as it was the first instrument with an appropriate electronic detector, which was able to give an acceptable compromise between good resolution and sufficient intensity of the measured powder diffraction pattern.^[53]

Indeed, there were many other instrumental developments in these decades. But due to the limited scope of this article they cannot be mentioned here. Additional information for the interested reader regarding the development of diffraction geometries and powder diffractometers can be found in the book of *Mittemeijer and Welzel*^[39] and in the publication of *Guinebrière et al.*^[57]

(c) The First (Powder) Diffraction Database

The idea of identifying chemical substances with powder X-ray diffraction was already proposed by *Hull* when he propagated the viewpoint that the powder diffraction method would serve as a new method for chemical analysis.^[20] In his publication in 1919 he stated the following:

“Further details concerning the theory of the production of these lines, and their relation to the crystalline structure of the substance, will be found in the Physical Review. This theory will not be reproduced here, as it is not essential to chemical analysis, beyond establishing the facts that every crystalline substance gives a pattern; that the same substance always gives the same pattern; and that in a mixture of substances each produces its pattern independently of the others, so that the photograph obtained with a mixture is the superimposed sum of the photographs that would be obtained by exposing each of the components separately for the same length of time. This law applies quantitatively to the intensities of the lines, as well as to their positions, so that the method is capable of development as a quantitative analysis.”

This idea of *Hull* was picked up by *Joseph Donald Hanawalt** [*Born July 6, 1902 in Royersford/Pennsylvania (United States), died June 26, 1987 Ann Arbor/Michigan (United States)], *Harold W. Rinn*, and *Ludo K. Frevel** [*Born May 31, 1910 in Frankfurt (Germany), died January 15, 2011 Bickford Cottage of Midland/Michigan (United States)] from Dow Chemical Company in Michigan. In 1936, *Hanawalt* and *Rinn* published an article, in which they introduced their classification system for powder diffraction patterns.^[58] This classification system consisted of a simple and quick determination of the positions of the diffracted lines, which allowed them to identify 1054 different chemical compounds (see Figure 6). Two years later in 1938, all three published an extensive article in which they supplied all intensity ratios and d-spacings of the most important diffraction lines for 1000 compounds.^[59]

(d) The Determination of the First Binary Non-cubic Crystal Structure

Probably the first determination of a binary non-cubic crystal structure from a powder diffraction experiment was made

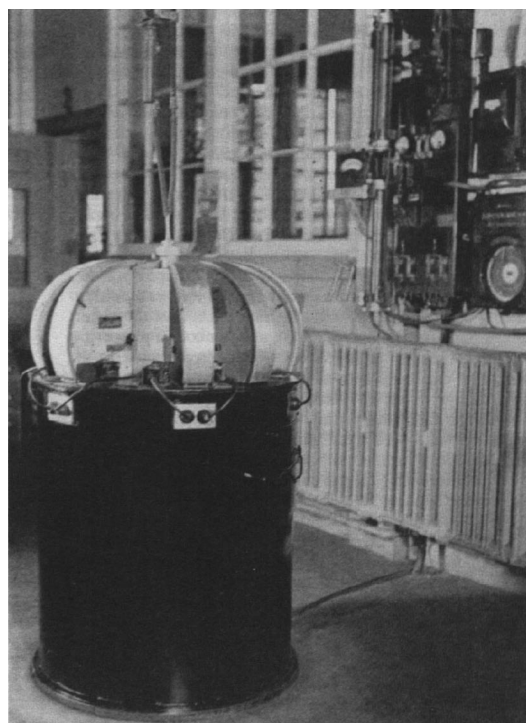


Figure 6. Powder diffraction unit. Original title: “*Diffraction apparatus and central board*”.^[59] On top of the black cylinder one can see the partial round film cassettes. Detailed information about this powder diffraction instrument can be found in *Hanawalt et al.*^[59]

by *William Houlder Zachariasen** [*Born February 5, 1906 in Langesund (Norway), died December 24, 1979 in Santa Fe/New Mexico (United States)] during the Manhattan Project of the United States in January and March 1944^[60,61] by careful investigations and by trial and error methods.^[10] Although the discovery was already made in the last years of the Second World War, it was part of the Manhattan Project and therefore classified information. Finally in 1948, *Zachariasen*’s work was declassified and he was able to publish the crystal structure of UCl_3 (space group $P6_3/m$) in “*The Journal of Chemical Physics*”^[61] and later in combination with other crystal structures in “*Acta Crystallographica*”.^[62]

(e) Neutrons Come into Play

In the course of the Manhattan Project further contributions beyond the work of *Zachariasen* were made and must be mentioned. In particular, the first experiments with neutron beams at the Clinton pile in Oak Ridge (Tennessee) (later Oak Ridge National Laboratory) and at the Chicago Pile 3 (CP-3) (later Argonne National Laboratory) have influenced materials science significantly.^[63] In 1944, the first neutron diffraction patterns of calcite single crystals were recorded {according to *Mason et al.*^[63] the first observation was done by *A. J. Ulrich* at the end of July 1944 with a single-axis spectrometer^[63,64] at the Clinton pile and by *Walter Henry Zinn** [*Born December 10, 1906 in Berlin (Kitchener)/Ontario (Canada), died February 14, 2000 in Clearwater/Florida (United States)] at the end of August 1944 at the CP-3 pile}. Although the first dif-

fraction patterns were of single crystals, a changeover to powders was a natural step, as it was stated by *Ernest Omar Wollan** [*Born November 6, 1902 in Glenwood/Minnesota (United States), died March 11, 1984 in Minnesota (United States)] and Clifford Glenwood Shull* [*Born September 23, 1915 in Pittsburgh/Pennsylvania (United States), died March 31, 2001 in Medford/Massachusetts (United States)] (who joined *Wollan* in June 1946^[64]) in the first unclassified publication about the topic in “Physical Review” in 1948:^[65]

“Experimental work on the diffraction of neutrons by crystals, directed towards obtaining information about the diffraction process and its dependence on the crystal and nuclear properties of various substances, was started at Clinton Laboratories in 1945 by E. O. Wollan and R. B. Sawyer. The first measurements along this line were made with single crystals; the results gave information regarding the phase of the nuclear scattering. It was found, however, that with single crystals it would be difficult to make measurements of the diffracted intensity with sufficient accuracy to permit reliable conclusions to be drawn regarding the effect on the intensity of various factors such as nuclear spin, presence of more than one isotope, characteristic temperature of crystals, crystal structure, etc.”

At the end of World War II, a two-axis spectrometer (see Figure 7), which was previously used by *Wollan* to study gases by X-ray scattering, was brought to the Clinton pile and mounted there.^[64] With this instrument it was possible to record the first powder diffraction patterns of polycrystalline NaCl, H₂O, and D₂O [later published in two articles of the same issue of Physical Reviews^[64,66] (see also Refs.^[67,68]). In the publications of 1948 one cannot find the first recorded powder neutron diffraction patterns as the patterns shown were

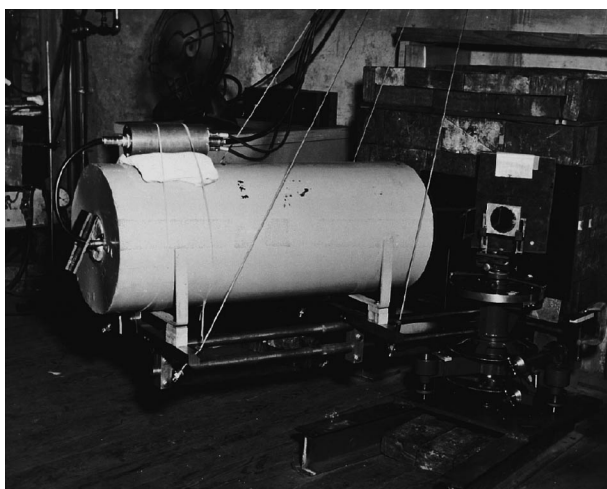


Figure 7. Two-axis neutron spectrometer for the collection of powder diffraction patterns at the Clinton pile.^[64] In his publication in 1995,^[64] Shull remembers: “Wollan had arranged for delivery to Oak Ridge of a base spectrometer that he had used in his earlier thesis work on x-ray gas scattering under Arthur Compton at Chicago. This spectrometer, with coaxial control of specimen and detector positions, had to be modified to support the larger loading of a neutron detector with its necessary shielding, and this was done with support cables running to a swivel-bearing in the ceiling directly above the spectrometer axis.”.

recorded at a later time. Fortunately in his review in 1995, *Shull* presented the first powder neutron diffraction pattern of NaCl, which is given in Figure 8.

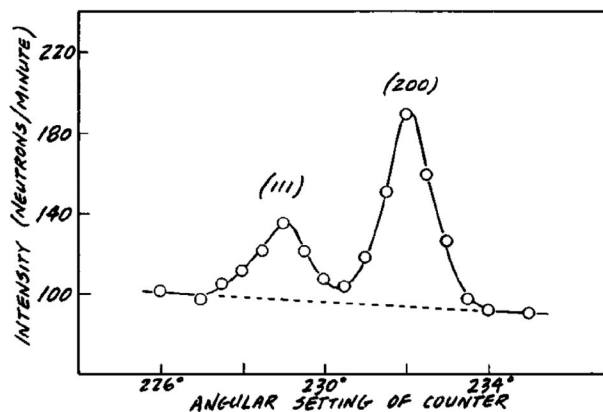


Figure 8. Portion of the first powder-diffraction pattern of NaCl taken at the Clinton pile.^[64]

In August 1949, *Shull* and *J. Samuel Smart* reported in a letter to the editor in Physical Review^[69] that they observed antiferromagnetic Bragg peaks, when they measured a powder sample of MnO (see Figure 9). This publication was followed

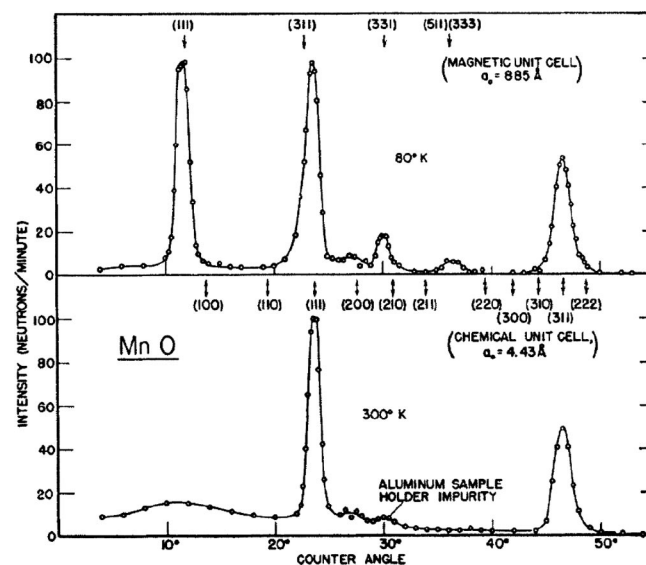


Figure 9. Neutron powder diffraction patterns of manganese oxide (MnO) at room temperature and at 80 K as observed by *Shull* and *Smart*.^[69] In their article they describe the picture and the appearance of the antiferromagnetic Bragg peaks as follows: “Figure 1 shows the neutron diffraction patterns obtained for powdered MnO at room temperature and at 80° K. The room temperature pattern shows coherent nuclear diffraction peaks at the regular face-centered cubic reflection positions and the liquid type of diffuse magnetic scattering in the background. It should be pointed out that the coherent nuclear scattering amplitudes for Mn and O are of opposite sign so that the diffraction pattern also shows the same nuclear diffraction peaks, since there is no crystallographic transition in this temperature region, and in addition shows the presence of strong magnetic reflections at positions not allowed on the basis of the chemical unit cell. The magnetic reflections can be indexed, however, making use of a magnetic unit cell twice as large as the chemical unit cell.”.

by another remarkable publication by *Shull, Wollan* and *W.A. Strauser*, in which they showed that the intensity of the ferrimagnetic (111) Bragg peak of a powder sample of Fe_3O_4 can be influenced by an applied magnetic field^[70] (see Figure 10). In July and in December 1951 they published another two papers, in which they showed in detail the antiferromagnetic and ferromagnetic neutron scattering of different compounds.^[71,72]

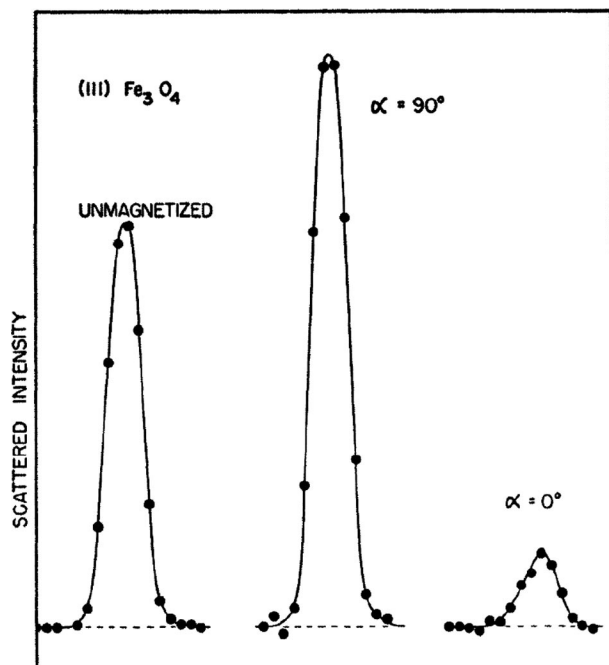


Figure 10. *Shull's, Wollan's and Strauser's* investigation of the (111) neutron powder diffraction peak of Fe_3O_4 .^[70] α is the angle between the scattering vector and the magnetization vector.

The Introduction of the Rietveld Method

The first step towards whole powder pattern fitting (WPPF) methods was done by *Hugo M. Rietveld** [*Born March 7, 1932 in The Hague (Netherlands)] in 1966, when he published the first successful attempt to use a least-squares algorithm with a refinement of the full-matrix to refine directly the background corrected integrated intensities of X-ray and neutron powder patterns^[73] (the information content which can be obtained from a powder diffraction pattern is schematically drawn in Figure 11). This algorithm was developed on a “big” Electrologica X1 computer with 8192 words (around 27.6 Kilobytes with a word length of 27 bit), which allowed a simultaneous refinement of up to 33 parameters including an “overall isotropic temperature factor, the overall scale factor and anyone of the individual isotropic temperature factors or atomic coordinates”.^[73] Unfortunately, the presentation at the Seventh Congress of the International Union of Crystallography in Moscow^[74] did not get wide recognition in the crystallographic community at that time, as *Rietveld* himself stated later in several review articles about his method.^[75–77] One year later in 1967, the next huge step was taken. *Rietveld* published the first WPPF analysis of tungsten trioxide (WO_3).^[78]

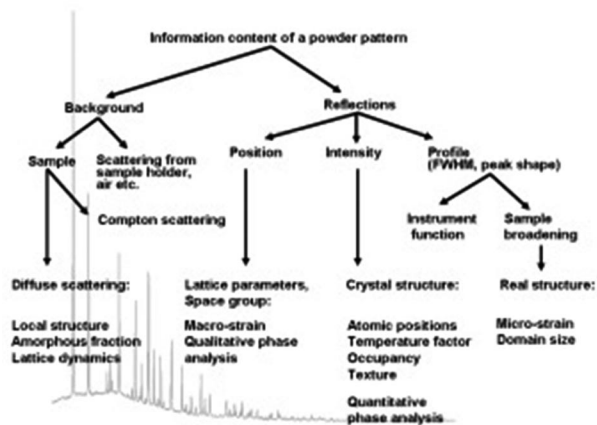


Figure 11. Schematic view of the information content of a powder diffraction pattern.^[84]

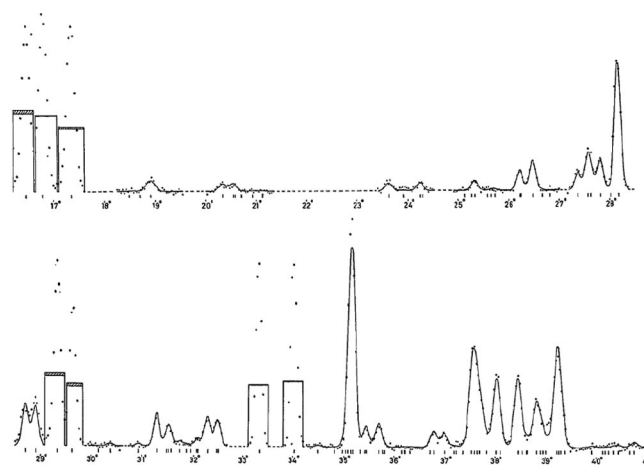


Figure 12. The first Rietveld refinement with a full peak profile in 1967. Original figure caption: “Neutron powder diffraction diagram of WO_3 (intensity vs. 2θ). The solid line indicates the calculated profile and the dots the measured intensities. The rectangles represent the integrated single-peak intensities, their different heights the agreement between calculated and observed values.”^[78]

In this short communication in “Acta Crystallographica”, he showed that with the assumption of a Gaussian profile for neutron Bragg reflections, one can refine almost completely overlapping reflections (see Figure 12) and more importantly, the standard deviation can be improved by an average factor of 2–3. At this time, wavelength, zero shift, and half-width values were not refined, but were directly taken from the powder diagram.^[75] Finally in 1969, *Rietveld* published his famous paper “A Profile refinement Method for Nuclear and Magnetic Structures” in the second volume of the “Journal of Applied Crystallography”.^[79] With the usage of an Electrologica X8 computer with 48,000 words (around 162 Kilobytes with a word length of 27 bit), it was possible to make a WPPF with the refinement of half-width parameters, zero shift, cell parameters, an asymmetry correction for the Gaussian shape at low angles, a preferred orientation correction, an overall scale factor, an overall isotropic temperature factor, fractional coordinates of the atoms in the asymmetric unit cell, atomic isotropic temperature

parameters, occupation numbers and, last but not least, the components of the magnetic vectors of each atom in the asymmetric unit cell. Additionally, it was now possible to introduce linear or quadratic constraints between the parameters in the least-squares algorithm. Another new development, which *Rietveld* made in this publication, was the introduction of residual values (R values), allowing for a quantitative judgment of the refinement quality. Most of the findings and equations, which *Rietveld* published are still used nowadays in their original form.

With this publication and the submission of 27 copies of his program to other institutes all over the world the reaction came.^[75] Within 8 years, 172 structures were refined from neutron powder diffraction data,^[75] before in 1977, the first WPPF with the Rietveld method was applied to X-ray diffraction data. In the same issue of the “Journal of Applied Crystallography”, three different groups published their results of Rietveld refinements on X-ray powder diffraction data. *Gunnar Malmros* and *John O. Thomas* as well as *Chandra P. Khattak* and *David E. Cox* used a modified Lorentzian to get a more appropriate peak shape model,^[80,81] in contrast to *Ray A. Young*, *Paul E. Mackie* and *Robert B. von Dreele*, who applied Gaussian and Cauchy functions in their refinement.^[82] What remains as one of the most impressive Rietveld refinements of X-ray powder diffraction data was conducted by *R. B. von Dreele* et al. when they solved and refined the first protein crystal structure (variant of the T_3R_3 human insulin-zinc complex with 1630 atoms in the asymmetric unit) from high-resolution synchrotron X-ray powder diffraction data^[83] (see Figure 13 for a synchrotron powder diffraction pattern of another protein).

The Post-Rietveld Era

The period between the first publications of *Rietveld* regarding his new WPPF method in the late 1960s and the international year of crystallography in 2014 is rich with instrumental and computational developments along with improvements in the field of powder diffraction. As these developments would certainly fill several books, we will try to give only a short overview and a few keywords in order to show the ways in which the field of powder diffraction has developed.

Worth mentioning are the contributions of *G. S. Pawley* in 1981^[86] and *Armel Le Bail* et al. in 1988,^[87] who developed whole powder pattern decomposition (WPPD) methods, which allow the extraction of integrated peak intensities which must be known in order to apply crystal structure determination by reciprocal or direct space methods.^[88] A major additional benefit of the WPPF methods is that the degree of peak overlap is reflected within the correlation matrix, which allows a judging of the reliability of the extracted integrated peak intensities.

Solving crystal structures is one of the most important issues in powder diffraction. In the last few decades different methods and algorithms have been developed to find ab initio structure solutions either with reciprocal space or direct space methods or even dual space methods.^[88,89] Some of the methods mentioned above were developed earlier than others and are

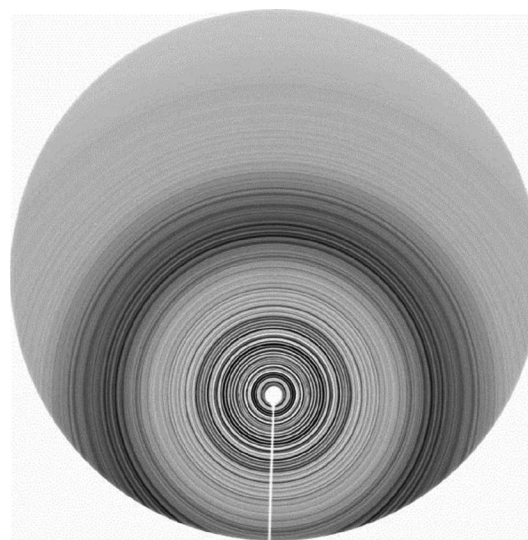


Figure 13. Example of Debye-Scherrer rings recorded with synchrotron radiation. Original figure caption: “Powder pattern of hen-egg white lysozyme obtained at 1-BM at the Advanced Photon Source at 20 keV using a MAR345 area detector positioned ~750 mm from the sample; ~9000 unique reflections are possible within the detection range ($d_{\min} \sim 1.85 \text{ \AA}$). A solvent-only background image has been subtracted to give this image.”^[85]

often derivatives of methods, which have already been used for single crystal analysis.

Reciprocal space methods, which were already developed for single crystals in the 1930s and which were boosted in the case of powder diffraction by the methods of *Pawley* and *Le Bail* are for instance the Patterson method,^[90] direct methods,^[91] difference Fourier analysis, Patterson search methods,^[92,93] the difference Patterson method aided by anomalous dispersion,^[94] the maximum entropy method,^[95–102] and the maximum likelihood method.^[98–103]

Direct space methods which developed along with increasing computational power are for instance grid search methods, the Distance-Least-Square (DLS) method,^[104] Monte-Carlo methods,^[105] simulated annealing,^[106,107] the pseudo-atom method^[88,108,109] and genetic algorithms.^[110–114]

Methods which operate in dual spaces are manifested in, for example, the charge-flipping algorithm.^[115–123]

Nowadays the method of simulated annealing as a representative of a global optimization method in direct space and charge-flipping as a representative of dual space methods are the most widely and successfully applied, owing to the continuously increasing computing powder (examples of solved crystal structures without and with simulated annealing can be found in Figure 14 and Figure 15, respectively).

The position of the atoms in a Rietveld refinement and also in structure solution methods as the simulated annealing approach can also be modeled by a different choice of the basis of the atomic configuration space. Traditionally, the basis of the atomic configuration space in a Rietveld refinement is built by using relative atomic coordinates. However, in the case of the refinement or the search for a solution of organic crystal structures with many light elements another choice is more

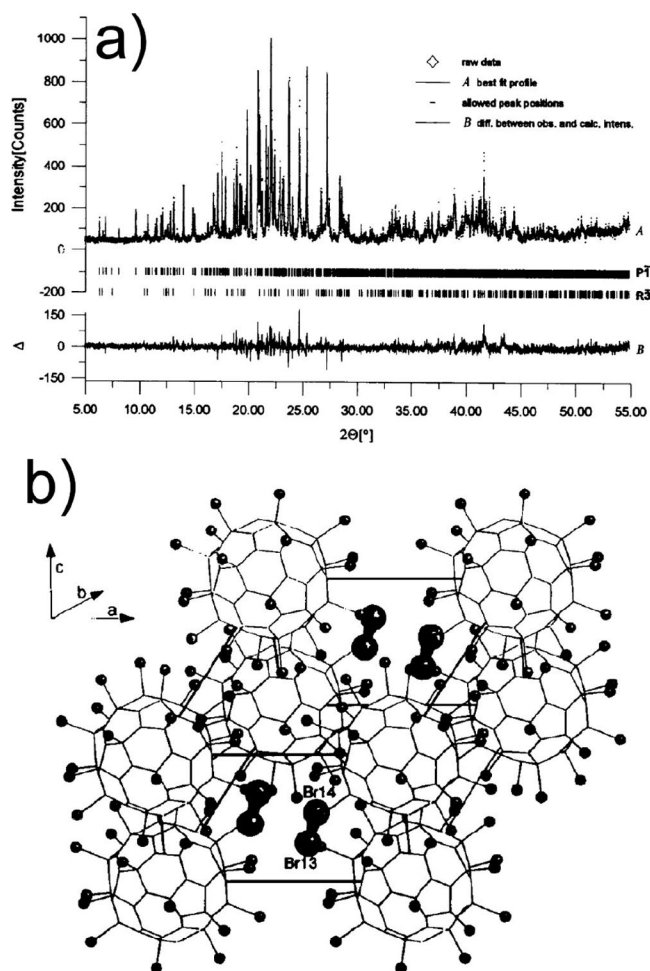


Figure 14. (a) Rietveld plot of the triclinic low-temperature phase of $C_{60}Br_{24}(Br_2)_2$ at 35 K.^[124] (b) Structure plot of the triclinic unit cell of $C_{60}Br_{24}(Br_2)_2$. The two free bromine molecules are drawn magnified for clarity.^[124] The solution of the crystal structure of this compound with 44 atoms in the asymmetric unit cell in 1995 is an example of the combination of different methods like Fourier and Patterson methods, rigid-body movements and grid search methods, before methods like simulated annealing and charge-flipping became widely available.

suitable. In these compounds the bond lengths and bond angles between individual atom species are well known as well as fragments of the organic molecule. Therefore, in these compounds it is more suitable to establish a rigid body and to use as basis of the atomic configuration space the rotations and translations of the rigid body and the dihedral angles and the bond lengths within the rigid body^[126–128] (Figure 15).

Another choice for the basis of the atomic configuration space can be made if the atomic coordinates are calculated from the amplitudes of symmetry modes or distortion modes of a distorted parent crystal structure, normally with higher symmetry.^[129–133] In general, it is also possible to use a combination of symmetry modes and rigid bodies within the same refinement or crystal structure solution process.^[134]

Apart from solving crystal structures from powder diffraction data, another important field in powder diffraction is the

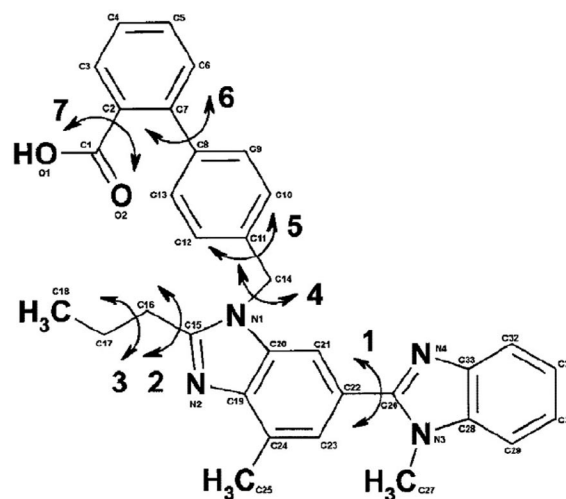


Figure 15. Structural formula of telmisartan (including the numbering scheme of the atoms) with the 7 torsion angles that were varied during the simulated annealing process.^[125] Additionally to the 7 torsion angles (internal degrees of freedom), 3 translational and 3 orientational parameters (external degrees of freedom) were included during the simulated annealing process to solve the A and B polymorphs from synchrotron powder X-ray diffraction data.^[125]

in situ investigation of powders. Nowadays, powders are investigated under many different conditions, for instance high and low temperatures, high pressure, irradiation by light or particles and also in different gas environments. In this context, powders are not only investigated by X-rays from laboratory sources, but also with X-rays from synchrotrons, neutrons from spallation sources or reactors, electrons, muons, etc.

The story of powder diffraction measurements at synchrotron sources began already in the seventies, when e.g. in 1976 *B. Buras, J. Staun Olsen, and L. Gerward* reported their first powder diffraction results (Figure 16), which they obtained using an energy-dispersive powder diffractometer set up at the Deutsches Elektronen-Synchrotron (DESY) in Hamburg/Germany.^[135] In the same year, *J. Bordas, A. M. Glazer, C. J. Howard, and A. J. Bourdillon* also performed an energy-dispersive powder diffraction experiment at the Daresbury synchrotron NINA in England.^[136] One year later in 1977, *Buras et al.*^[137] reported the first in situ synchrotron powder diffraction experiments [high temperature experiments on α - and β -manganese and high pressure experiments on tellurium oxide (TeO_2)], which were carried out by using energy-dispersive diffraction. In 1978, the first refinement of energy-dispersive powder diffraction data was performed by *Glazer et al.*^[138] Three years later in 1981, *Thompson et al.* demonstrated at the ADONE storage ring in Italy that Debye-Scherrer photographs of Al_2O_3 (corundum) can be obtained by using monochromatic synchrotron radiation.^[139] The resolution, which they claimed in their publication, was $\Delta d/d \approx 1.4 \times 10^{-3}$ (at $2\theta = 100^\circ$) for a Debye-Scherrer camera with radius 57.3 mm and $\Delta d/d \approx 3.5 \times 10^{-4}$ (at $2\theta = 100^\circ$) for a Debye-Scherrer camera with radius 239 mm.^[139] In 1983, a Debye-Scherrer setup with the first Si(111) analyzer crystal was constructed by *Cox et al.*^[140] at the Cornell High Energy Synchrotron Source (CHESS) in

the United States, which had a resolution of approximately $\Delta d/d \approx 5.0 \times 10^{-4}$ (at $2\theta \approx 100^\circ$) (see Figure 4 in^[140]). During the course of their investigations, they also carried out the first Rietveld refinement of synchrotron powder diffraction data on a Bi_2O_3 powder pattern obtained from their Debye-Scherrer setup.^[140] Different analyzer crystals were investigated by the same authors in a later study.^[141] Nowadays the resolution of synchrotrons is of the order of $\Delta d/d \approx 1.5 \times 10^{-4}$ at 10 keV [for example at the ID22 (former ID31) beamline at ESRF/Grenoble or at the I11 beamline at Diamond/Oxfordshire]. Among the first crystal structures to be solved from synchrotron powder diffraction data was BeH_2 by Smith et al. in 1988.^[142] Further information about the history of synchrotron light sources and the first diffraction experiments can be found in the reviews of Holmes and Rosenbaum,^[143] Helliwell,^[144] and Paszkowicz.^[7]

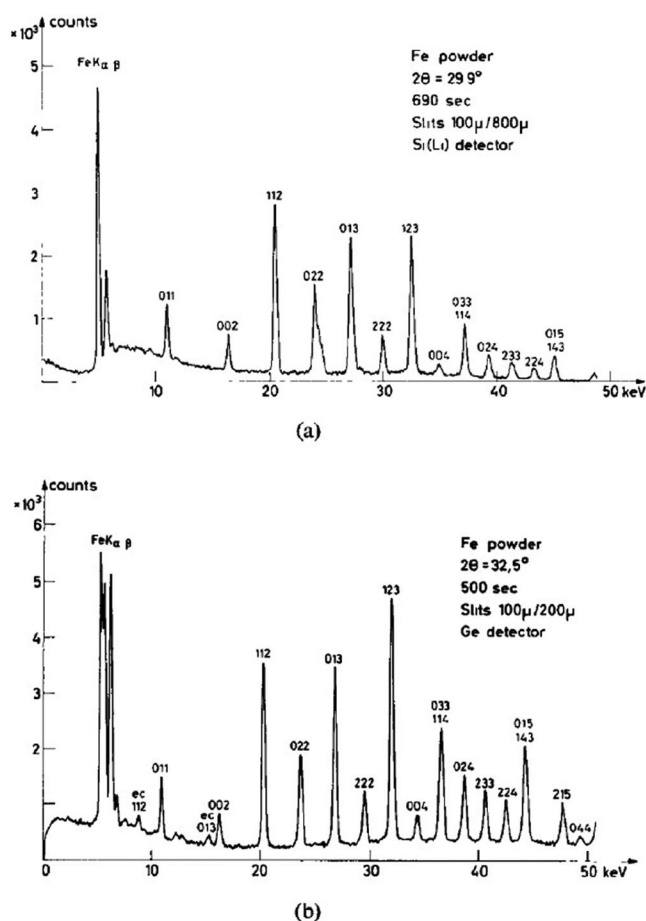


Figure 16. Presumably first powder diffraction patterns obtained by energy-dispersive synchrotron diffraction. Original figure caption: “Energy-dispersive diffraction spectrum of iron powder, recorded with (Si(Li) detector and Ge detector, respectively; slit widths are given for S1 and S2; ec = escape peaks. In addition to the diffraction lines some fluorescence lines are seen.”^[135]

Today the investigation of powders by synchrotron radiation with powder diffraction methods had become a standard procedure used by hundreds of scientists per year all over the world. Nowadays the data acquisition is often highly automated, only interrupted by changing environmental parameters

or by changing of samples (some synchrotron beamlines provide automatic sample changing by robots). In a few hours it is possible to collect dozens or even hundreds of powder patterns. This is especially true in the case of the most modern synchrotrons where one can collect a powder pattern at almost every second, which produces a huge number of data sets.

The subsequent sequential refinement of all of these data sets is very time consuming and fitting of individual parameters with physical, chemical or empirical equations is often done afterwards. In 2007, Graham W. Stinton and John S. O. Evans published an article in which they showed how the parametric treatment of several powder diffraction data sets can be carried out.^[145] This so-called parametric or surface Rietveld refinement has two benefits. The first is that the subsequent fitting of individual parameters with the above mentioned equations is avoided, as the fitting can be already done by applying the least-squares algorithm within most of the crystallographic software packages. The other effect is that the application of physical, chemical or empirical equations can stabilize the refinement and helps to avoid the occurrence of false minima within the refinement.

Since the beginning of the new millennium, more and more information from a powder diffraction pattern can be extracted (Figure 10). In the 1990s the basis of the fundamental parameter approach was laid down, which models the peak shape on the basis of physical effects with respect to the instrumental conditions.^[146–150] The modeling of the peak shape is becoming more and more important, as the peak shape also provides lots of information about the microstrain^[151] and other microscale effects (see also books of Mittemeijer and Welzel,^[37] Mittemeijer and Scardi,^[54] and Dinnebier and Billinge^[84]).

Another approach to extracting the maximum information from a powder pattern is to calculate the pair distribution function (PDF).^[152] With the PDF it is possible to see directly the different interatomic distances which occur in a certain compound.

Regarding the information content of a powder diffraction pattern, the quantitative phase analysis (QPA) methods must also be mentioned. Early attempts to use the Rietveld method for QPA were made by R. J. Hill and C. J. Howard in 1987^[153] and by D. L. Bish and S. A. Howard in 1988.^[154] To date, the development of software which can automate this kind of analysis is still a very important issue as QPA is used in all kind of applied sciences, for instance in mineralogy, pharmacy, and forensics. Methods like the partial or no known crystal structure (PONKCS) method^[155] work very well and even allow the precise determination of the phase amount of a compound with an unknown crystal structure.

Conclusions

From the “birth” of powder diffraction with the first experiments of Debye, Scherrer, and Hull through the invention of the Rietveld method to today, where we can use exhaustive investigation methods to solve crystal structures using modern computers, almost a whole century has passed. At the beginning, the investigations of crystal structures were very time

consuming and calculations were done by hand. Most of the crystal structures, which were solved at that time, possessed cubic or hexagonal symmetry. Since the fifties, the continuous development of computers has also led to a continuous development of new methods and algorithms, especially in the field of powder diffraction. Nowadays, huge crystal structures with hundreds or sometimes thousands of atoms can be measured and solved or at least refined within one day, applying different direct space or dual space methods in every crystal system. The usage of synchrotron and neutron sources became routine, as they support laboratory measurements, which are recorded on thousands of laboratory powder X-ray diffractometers worldwide.

The ongoing developments in computational power as well as the development of diffractometers with more brilliance and higher resolution will continue to stimulate the field of powder diffraction. The development of new software and algorithms will open the field even to non-experienced users, making powder diffraction the method of choice for the investigations of many solid state materials.

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