Chapter 1
Powder Diffraction: By Decades

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Abstract This introductory chapter reviews the first 100 years of powder diffraction, decade by decade, from the earliest X-ray powder diffraction measurements of the crystal structure of graphite through to the diversity and complexity of twenty-first century powder diffraction. Carbon features as an illustrative example throughout the discussion of these ten decades from graphite and the disorder of carbon black through to lonsdaleite, the elusive hexagonal polymorph of diamond, and C_{60}, the most symmetrical of molecules. Electronics and computing have played a leading role in the development of powder diffraction, particularly over the past 60 years, and the Moore's Law decade-by-decade rise in computing power is clear in the increasing complexity of powder diffraction experiments and material systems that can be studied. The chapter concludes with a final discussion of decades – the four decades of length-scale from the ångstrom to the micron that not only represent the domain of powder diffraction but are also the distances that will dominate twenty-first century science and technology.

1.1 Powder Diffraction – The First 100 Years

1.1.1 A Brief Preamble

The origins of X-ray diffraction can be traced back to the discovery of X-rays by Wilhelm Conrad Roentgen in the University of Wurzburg in the summer of 1895 [1]. The dramatic early images of the bones of living hands (initially, those of his wife!)

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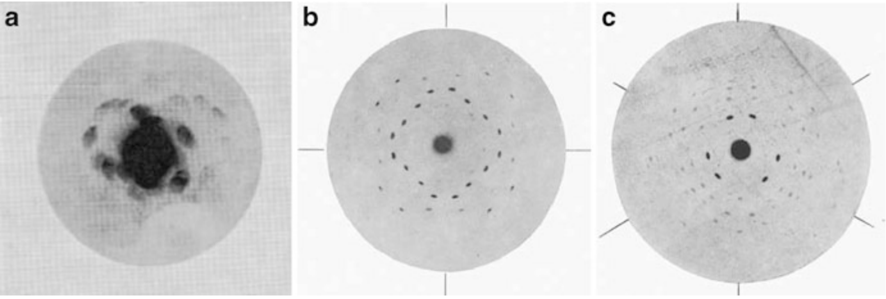


Fig. 1.1 (**a**) Friedrich and Knipping's first successful X-ray diffraction photograph – the crystal was copper sulphate; (**b**) and (**c**) zinc-blende Laue photographs along the four-fold (**b**) and three-fold (**c**) axes from Laue, Friedrich and Knipping, *Sitz. Ger. Bayer. Akademie d. Wiss*, 8 June 1912

created an immediate sensation and, even before the turn of the century, medical applications were quickly developed. Perhaps less well-known was Roentgen's repeated attempts to observe the phenomenon of X-ray diffraction – and he was most likely successful, as his Third Communication on X-rays in March 1897 suggests, in observing diffraction on a few fleeting occasions. Roentgen moved from Wurzburg to Munich in 1900 and in 1901 was accordingly awarded the first Nobel Prize in Physics. The University of Munich was one of the leading universities in the world in the "new physics" and rapidly became the centre of the development of X-rays physics with a roll call of names such as Sommerfeld, Groth, Debye, Ewald and Laue that would define much of the early years of the subject. Laue arrived in Munich in 1909 with interests that ranged across the whole of physics from special relativity and optics to thermodynamics and the theory of radiation. Prompted by Ewald, Laue's intuition led him to an analysis of the first diffraction data collected by his assistants, Friedrich and Knipping. The first diffraction pattern (Fig. 1.1a) was essentially uninterpretable but within weeks the improvement in data quality was not only remarkable but, crucially, also led to an interpretable solution [2] (Fig. 1.1b, c) and the 1914 Nobel Prize in Physics – but only to Laue! The first crystal structure is, however, attributed to the father and son team, W.H. and W.L. Bragg.

On October 18, 1912, only a few months after the first diffraction patterns had been successfully collected, the elder Bragg published his first paper [3] offering an interpretation of the zinc-blended diffraction data published by Laue, Friedrich and Knipping. It was, however, the younger Bragg who, while still a student at Cambridge, came up with a correct analysis of the origins of the diffraction data [4]. Shortly afterwards, the Braggs collected single crystal data and solved the crystal structures of NaCl, KCl, KBr and KI [5] – four crystal structures in the first paper and the Nobel Prize in Physics within 2 years in 1915! Powder diffraction, with its lower intensities, had to wait only a little longer. Some of the first clues are to be found in the 1914 Nobel Prize lecture [6] delivered by Max von Laue who said "Since 1912 much has been done in both fields, and in both sectors W.L. Bragg and W.H. Bragg have taken the first important step beyond the investigations carried out

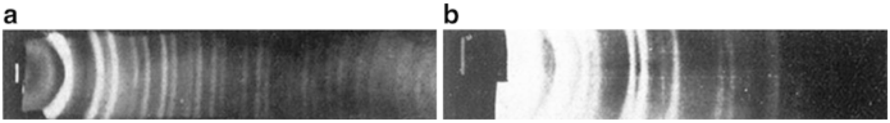


Fig. 1.2 Powder diffraction photographs of (**a**) diamond and (**b**) graphite (Hull 10)

at Munich. It would range far too wide if I were, at this juncture, to compile a fairly comprehensive list of all the researchers who have gained distinction in that research work. I can mention here only the transformation of the process, which proved to be of great importance for the further conduct of the experiments and in which Debye transferred the examination of beautiful, well-formed crystal fragments – which sometimes are obtainable only with considerable difficulty – to research into the finest possible crystal powder."

1.1.2 The First Powder Diffraction Measurements

X-ray powder diffraction has two separate beginnings in Germany, again in Munich, and almost simultaneously in the United States. In Munich, Peter Debye determined that not only powders but also liquids should exhibit distinctive diffraction patterns [7]. Along with Paul Scherrer, Debye performed the first powder diffraction measurements [8] discovering, inter alia, the crystal structure of graphite. The first measurements in the United States happened in very different circumstances – not in a university but in the General Electric Research Laboratory (GERL) in Schenectady, New York by Albert Hull [9]. A chance comment about the unsolved structure of iron by W.H. Bragg, who visited GERL in 1914, drew Hull into the field of X-ray structural analysis and rapidly, although World War 1 interrupted his efforts, he developed many of the essentials of the powder diffraction technique using photographic techniques (see Fig. 1.2) and discussed multi-phase analysis, preferred orientation, the need for sample rotation, wavelength filters, absorption, the importance of sample preparation and the concept of a "lattice constant". The three principal papers [10–12] that Hull published are significant tours-de-force – his first paper alone described the correct crystal structures of iron, silicon, aluminium, magnesium, sodium, lithium, nickel, diamond and graphite. While Debye and Scherrer reported the 3R structure of graphite (space group *R-3m* with hexagonal lattice constants, $a = 2.516$ Å and $c = 10.206$ Å), Hull reported the more familiar 2H structure which adopts space group $P6_3/mmc$ with $a = 2.47$ Å and $c = 6.80$ Å.

Hull, like Debye, did not stay long in powder diffraction research (indeed, his short time in powder diffraction was essentially a diversion from his research on thermionic valves) but moved on in GERL to invent, among other things, the magnetron which was later used not only to create the microwave oven but also by the British military in the development of radar.

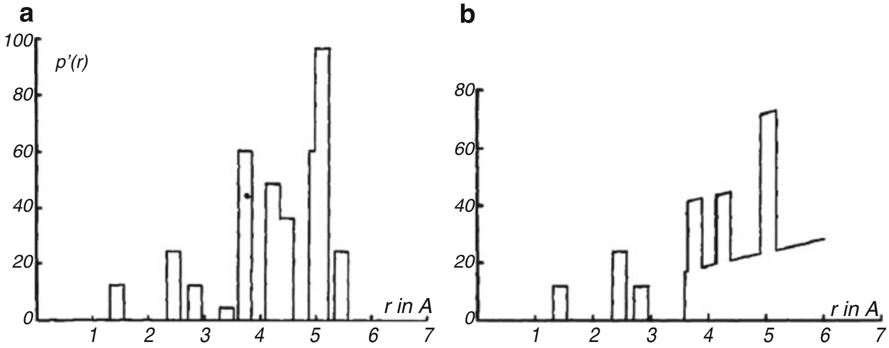


Fig. 1.3 (**a**) Atom distribution in a graphite crystal and (**b**) Atom distribution in carbon black, "a mesomorphic form of carbon, consisting of single graphite layers stacked roughly parallel to one another" [15]. It is noteworthy that while the data are not of the quality obtained with modern instrumentation, the experimental and analytical rigour are all of a standard to aspire!

1.1.3 Towards Disorder

Crystallography developed rapidly in the 1920s and 1930s with an increasing awareness of the power of the technique, particularly when single crystals were available. Powder diffraction, although a powerful tool for fingerprinting and phase identification, suffered (and still does) from a paucity of information compared with what is available from single crystal data. One person deserves a special mention in the development of the powder diffraction technique over the next 30 years and he took the technique in the direction of disorder. Carbon, again, is the principal element of the story; Bertram Warren [13, 14] was the scientist. The Fourier Inversion Method, which provides the pair distribution function, had applied to the diffraction patterns of glass, and Warren was keen to apply the method to other forms of amorphous matter. Carbon black was presumed to be amorphous and Warren collected data from a sample that happened to be in the laboratory. Knowing that carbon black diffracted poorly, he discovered, to his surprise, that the diffraction pattern, when Fourier inverted to provide the atom-atom separations, resulted in a distribution that was remarkably similar to graphite (Fig. 1.3). He concluded, in his first paper on the subject published in 1934 [15], that carbon black was not a truly amorphous form of carbon stating that "the existence of single graphite layers is very definite and therefore the material is at least mesomorphic. The diffraction data indicate a heterogeneous mixture containing particles which range from single graphite layers up to graphite crystals several layers thick." It was a topic that he returned to throughout his career [16–18] – his last carbon-black paper was published in 1965.

Very significantly, Warren discovered that materials did not fit into neatly defined categories of crystalline and amorphous. Powder diffraction is not simply the domain of crystalline systems – or should not be – and a major objective of this

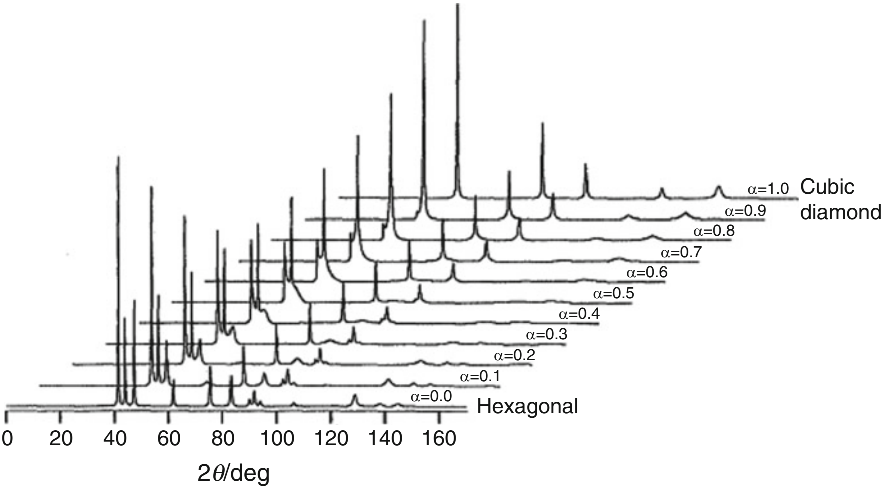


Fig. 1.4 Montage of powder X-ray diffraction patterns calculated as a function of the probability that layers in a diamond crystal will stack in the cubic diamond sequence. Thus $\alpha = 0$ corresponds to pure lonsdaleite and $\alpha = 1$ corresponds to pure diamond [19]

school is to remove the artificial boundaries in the solid-state between crystalline, poorly crystalline and amorphous. Powder diffraction is not synonymous with the Rietveld method – but we are ahead of ourselves – that is the next topic!

As a postscript to this section, it is worth noting that there has been significant subsequent development in the analysis of disordered and partially ordered systems. Deem et al. (1991) [19] produced an elegant program for calculating the diffraction patterns of faulted and strained crystals. Figure 1.4 continues the theme of carbon and illustrates the continuous variation of diffraction pattern from diamond to lonsdaleite, the hexagonal variant of diamond. The peak broadening and appearance and disappearance of peaks are particularly noteworthy. Other major developments have been reviewed by Egami and Billinge [20] and Scardi et al. [21].

1.1.4 Neutron Powder Diffraction and the Rietveld Method

The first neutron diffraction experiments were performed in 1945 by Ernest O. Wollan using the Graphite Reactor at Oak Ridge National Laboratory, USA. He was joined shortly afterwards (June 1946) by Clifford Shull, and together they established the basic principles of the technique and applied it successfully to many different materials, addressing problems such as the structure of ice and the microscopic arrangements of magnetic moments in materials [22]. For this achievement, Shull was awarded one half of the 1994 Nobel Prize in Physics with Bertram Brockhouse (who received the reward for his research on neutron triple-axis spectrometers and inelastic neutron scattering). Wollan died in 1984 and did not receive the prize that was rightfully his. It is said that the unusually long delay in awarding the prize was due to the politically incorrect association of neutron diffraction analysis with nuclear power!

While Shull and Wollan performed the first neutron powder diffraction measurements, the most significant contribution from neutron diffraction is almost certainly the development of the structure refinement using the full diffraction profile by Hugo Rietveld in the late 1960s [23, 24]. Fame is assured when one's name becomes an adjective and the technique that is ubiquitous today and has enabled the development of the full power of the powder diffraction method is, of course, now called the Rietveld method [25]. Rietveld's two principal papers [23, 24] are elegantly written and the abstract of his 1969 paper succinctly describes the challenge and his solution.

"A structure refinement method is described which does not use integrated neutron powder intensities, single or overlapping, but employs directly the profile intensities obtained from step-scanning measurements of the powder diagram. Nuclear as well as magnetic structures can be refined, the latter only when their magnetic unit cell is equal to, or a multiple of, the nuclear cell. The least-squares refinement procedure allows, with a simple code, the introduction of linear or quadratic constraints between the parameters."

Rietveld's original program not only enabled the refinement of chemical and magnetic structures but also contained constraints, preferred orientation, peak asymmetry, essentially all the current definitions of R-factors, and the generally used formulation of F_{obs}. He even stated that the method can, in principle, also be extended to X-ray powder diagrams, if a satisfactory function can be found to describe the peak profiles. This had to wait a further decade and then, as with the beginnings of powder diffraction, two groups [26, 27] independently adapted the technique to X-ray data. Malmros and Thomas in the University of Uppsala, Sweden applied the Rietveld method to Guinier-Hagg film data while Khattak and Cox at Brookhaven National Laboratory, USA, demonstrated its feasibility with a conventional focussing X-ray powder diffractometer.

1.1.5 Back to Carbon

The principal purpose of this introductory talk has been to present a short – and very selective – history of the development of powder diffraction. Modern powder diffraction – the topic of this 44th International School of Crystallography – spans an enormous breadth of topics [28–31] from archaeology and applied engineering through to pharmaceutical science and protein crystallography. Given this range of modern powder diffraction, it is probably best to finish the story a few years ago. Carbon, in the form of graphite, carbon black, diamond and lonsdaleite have all featured in the decades of powder diffraction and so it is appropriate to finish with the crystal structure of C_{60}, buckminsterfullerene, the most symmetrical of all molecules.

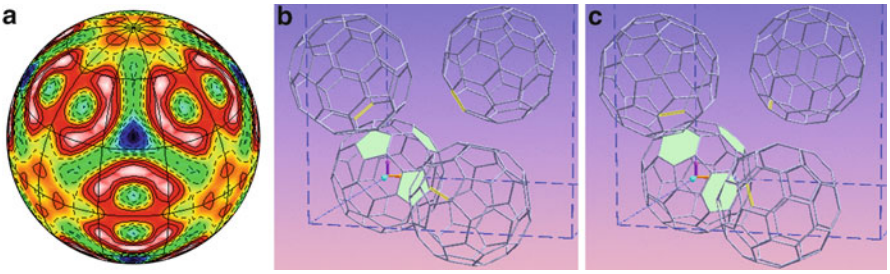


Fig. 1.5 (After [37]) (**a**) the orientation distribution function in the orientationally disordered high temperature phase. *White* represents excess density and *blue* low density – the overall deviation from spherical symmetry is only *ca.*10%; (**b**) and (**c**) the two distinct C_{60} orientations in the low-temperature phase. The orientation with pentagons (**b**) aligned along ∼110 directions pointing towards the C=C bonds are lower in energy than the "hexagon" orientation (**c**). This energy difference is calculated from powder diffraction data alone (color figure online)

C_{60} was first identified in a molecular beam in 1985 by Kroto and colleagues [32] who confirmed its truncated dodecahedral shape and icosahedral symmetry. However, it was the discovery of a synthesis route for bulk C_{60} [33] that led to the dramatic development of fullerenes and subsequently carbon nanotubes. The crystal structure was soon identified to adopt a face-centred cubic lattice [34–36] that contained orientationally disordered molecules at room temperature which ordered below 249 K to a primitive cubic *Pa3* symmetry. Neutron powder diffraction measurements [37] not only determined the subtle deviations from spherical behaviour in the high temperature phase (Fig. 1.5a) but also revealed an orientational glass transition which was explained by the presence of two crystallographically distinct orientations (Fig. 1.5b, c).

The most symmetrical of molecules is itself two-fold disordered in the ordered low-temperature phase and this disorder is paradoxically a consequence of the very high molecular symmetry. More recent neutron powder diffraction analysis [38] has not only obtained very precise measurements of these orientations at 4 K but has also determined the single and double bond lengths to an extreme precision (see Table 1.1) and modelled the orientational single-particle diffuse scattering (Fig. 1.6). These latest results would not have been possible without substantial developments in instrumentation, driven in significant part by advances in electronics (see Sect. 1.2), but also by progress in powder diffraction software – in this case, specifically the implementation of computer algebra in TOPAS [39] (see Table 1.2).

1.2 Powder Diffraction – The Power of Moore's Law

The previous section noted the importance of advances in computing power in the development of the powder diffraction method. It would have been impossible to utilise the Rietveld method without computers and early measurements were

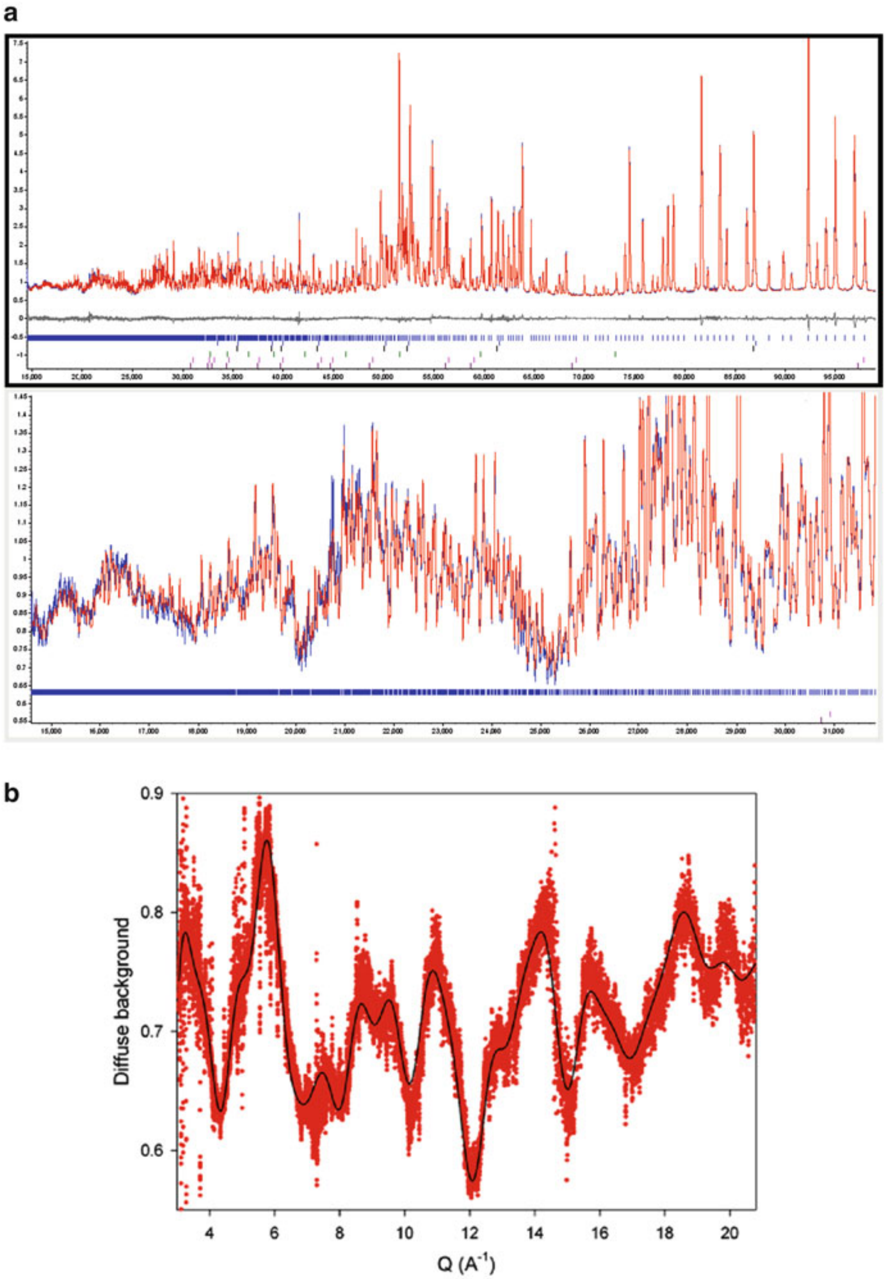


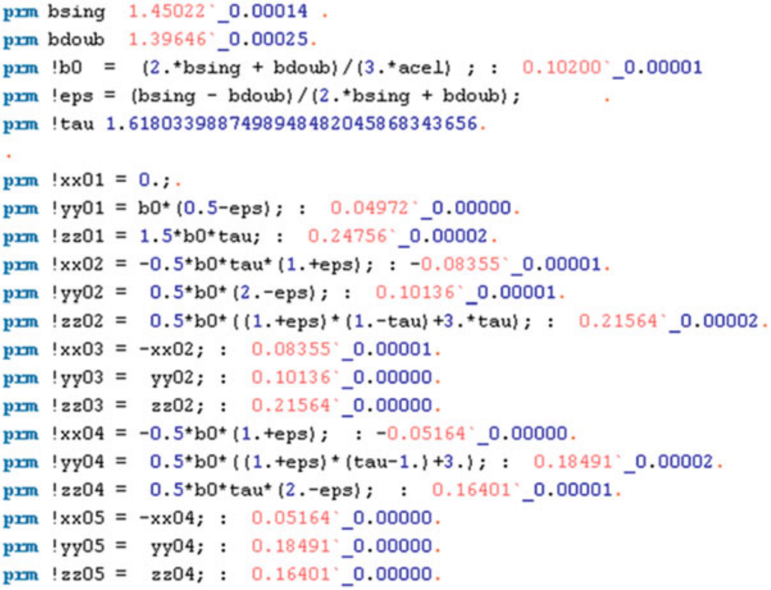
Fig. 1.6 (**a**) Observed and calculated 2007 HRPD neutron powder diffraction of C_{60} at 4 K (*top*) the full range of data from 0.3 to 2.0 Å and (*bottom*) the new range available in 2007 from 0.3 to 0.6 Å containing ∼1,500 new reflections, (**b**) the background fitted in TOPAS as part of a Rietveld refinement using a single molecule diffuse scattering model to a Q_{max} of 21 $Å^{-1}$ [38]

Table 1.1 Structural data for C_{60} obtained from HRPD, ISIS in 1991 and 2007

Year	a (Å)	b_d(Å)	b_s(Å)	ϕ_p (°)	ϕ_h (°)	n_p
1991	14.04212(4)	1.391(18)	1.455(12)	98 (fixed)	38 (fixed)	0.838(2)
2007	14.04225(2)	1.39745(30)	1.44953(15)	99.751(3)	41.915(15)	0.8276(9)

a, b_d and b_d are the 4 K lattice constant and double and single bond lengths while ϕ_p,ϕ_h and n_p are the rotation angles along 111 for "pentagon" and "hexagon" orientation and the fraction of "pentagon" orientation at 5 K. The increase in 2007 precision is a consequence of the larger Q range and also the refinement parameterisation

Table 1.2 Part of the TOPAS input file for the 4 K refinement of C_{60} that defines all atomic positions in the standard orientation based solely on C–C and C=C bond lengths. A single rotation angle C_{60} is required to define the atomic coordinates of each of the "pentagon" and "hexagon" orientations. The script highlights the power of computer algebra in TOPAS to define the refinement in terms of the appropriate parameters [38]



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prm bsing  1.45022`_0.00014 .
prm bdoub  1.39646`_0.00025.
prm !b0  =  (2.*bsing + bdoub)/(3.*acel) ; :  0.10200`_0.00001
prm !eps = (bsing - bdoub)/(2.*bsing + bdoub);        .
prm !tau 1.6180339887498948482045868343656.

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prm !xx01 = 0.;.
prm !yy01 = b0*(0.5-eps); :  0.04972`_0.00000.
prm !zz01 = 1.5*b0*tau; :  0.24756`_0.00002.
prm !xx02 = -0.5*b0*tau*(1.+eps); : -0.08355`_0.00001.
prm !yy02 =  0.5*b0*(2.-eps); :  0.10136`_0.00001.
prm !zz02 =  0.5*b0*((1.+eps)*(1.-tau)+3.*tau); :  0.21564`_0.00002.
prm !xx03 = -xx02; :  0.08355`_0.00001.
prm !yy03 =  yy02; :  0.10136`_0.00000.
prm !zz03 =  zz02; :  0.21564`_0.00000.
prm !xx04 = -0.5*b0*(1.+eps);   : -0.05164`_0.00000.
prm !yy04 =  0.5*b0*((1.+eps)*(tau-1.)+3.); :  0.18491`_0.00002.
prm !zz04 =  0.5*b0*tau*(2.-eps);   :  0.16401`_0.00001.
prm !xx05 = -xx04; :  0.05164`_0.00000.
prm !yy05 =  yy04; :  0.18491`_0.00000.
prm !zz05 =  zz04; :  0.16401`_0.00000.
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restricted by both the computer speed and also the extremely small computer memories compared with modern-day machines. Initially, a single cycle of Rietveld analysis could be measured in hours and diffraction data collection was limited to a few thousand datapoints per day. Figure 1.7 shows the increase in data collection rates for neutron powder diffraction instruments since 1947. The graph follows an exponential Moore's Law growth suggesting that computer memory is the limiting factor, rather than neutron sources, at the frontiers of neutron scattering. Time-of-flight instruments such as GEM and WISH require massive raw files for collecting data as a function of both scattering angle and time of flight. These instruments

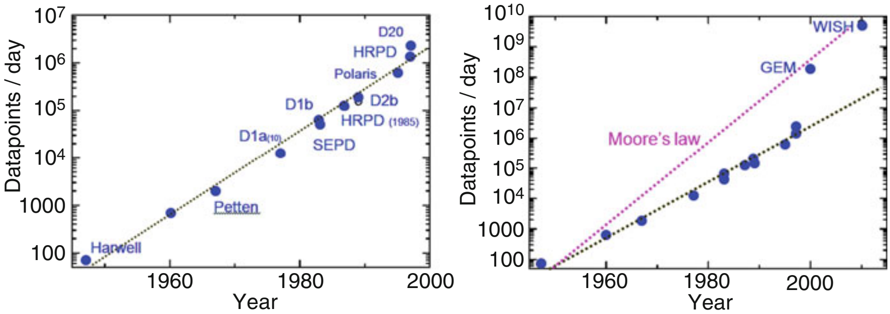

Fig. 1.7 The exponential rise in raw data collection rates for neutron powder diffraction. The early measurements at Harwell by George Bacon were written down by hand – around 100 data points were collected each day. The Petten measurements are attributed to Hugo Rietveld and mark the beginning of the Rietveld method

would be impossible to build and operate without massive data storage and rapid data reduction facilities. The ability to store and collate data rapidly is also crucial in the development of ultra-fast X-ray powder diffraction measurements.

1.3 The Four Most Important Decades – From the Ångstrom to the Micron – The Domain of Powder Diffraction

In the previous sections, we have discussed the development of powder diffraction over the decades of the twentieth century and emphasised the central importance of the decades of growth in computer speed and memory. However, the decades of the twentieth century have not only transformed powder diffraction but all of science and this has been fuelled by the growth in electronics that has taken us, within the span of a single scientific career, from kilobytes to megabytes, gigabytes, terabytes and, just over the horizon, petabytes. But there is another set of decades, the decades of length scales that are also worthy of mention. The shortest length-scale that has meaning in our universe is the Planck length, $\ell_P = \sqrt{(\hbar G/c^3)}$, which represents the granularity of space itself. Coming in at around 1.6×10^{-35} m., it is unbelievably small and, of course, at present is a conjecture and not proven. The smallest distance that has been measured and probed comes in at $\sim 10^{-20}$ m., around 10^{-5} of the diameter of a proton. This is, of course, the domain of particle physics which represents our quest to understand the fundamental particles and interactions and the underlying laws that govern our universe. At the other length of the length spectrum is the dimension of the visible universe itself. Multiplying the estimated age of the universe, 13.75 ± 0.11 billion years, by the speed of light leads to a massive 1.3×10^{26} m. This is domain of astronomy and cosmology where we can observe and understand but cannot touch nor change. Within the 61 orders of magnitude from the Planck length to the size of the visible universe, there are four decades from the ångstrom to the micron that already dominate the science of the twenty-first century and will continue to define our future technological developments. The ability to synthesise, visualise, understand and modify objects on these length-scales place powder diffraction, along with other techniques such as electron microscopy, at the centre of the discovery and development of twenty-first century science and technology.

References

1. http://www.iucr.org/publ/50yearsofxraydiffraction
2. Friedrich W, Knipping P, von Laue M (1912) Interferenz-Erscheinungen bei Röntgenstrahlen. Sitzungsberichte der Mathematisch-Physikalischen, Classe der Königlich-Bayerischen Akademie der Wissenschaften zu München, pp 303–322
3. Bragg WH (1912) The specular reflexion of X-rays. Nature 90:410
4. Bragg WL (1913) The diffraction of short electromagnetic waves by a crystal. Proc Camb Phil Soc 17:43
5. Bragg WH (1913) The reflection of X-rays by crystals (II). Proc R Soc Lond A 89:246–248; Bragg WL (1913) The structure of some crystals as indicated by their diffraction of X-rays. Proc R Soc Lond A 89:248–277; Bragg WH, Bragg WL (1913) The structure of the diamond. Proc R Soc Lond A 89:277–291
6. von Laue M (1915) Concerning the detection of X-ray interferences, Nobel lecture, http://nobelprize.org/nobel_prizes/physics/laureates/1914/laue-lecture.pdf
7. Debye P (1915) Scattering of X-rays. Ann Physik 46:809–823
8. Debye P, Scherrer P (1916) Interferenzen an regellos orientierten Teilchen im Rontgenlicht. Physik Z 17:277–282
9. http://www.iucr.org/__data/assets/pdf_file/0015/771/hull.pdf
10. Hull AW (1917) A new method of X-ray crystal analysis. Phys Rev 10:661–696
11. Hull AW (1919) A new method of chemical analysis. J Am Chem Soc 41:1168–1175
12. Hull AW (1921) The X-ray crystal analysis of thirteen common metals. Phys Rev 17:571–588
13. http://ww1.iucr.org/people/warren.htm; http://www.iucr.org/__data/assets/pdf_file/0020/785/warren.pdf
14. Warren BE (1969/1990) X-ray diffraction. Addison-Wesley/Dover, Reading/Mineola
15. Warren BE (1934) X-ray powder diffraction study of carbon black. J Chem Phys 2:551–555
16. Biscoe J, Warren BE (1942) An X-ray study of carbon black. J Appl Phys 13:364–371
17. Houska CR, Warren BE (1954) X-ray study of the graphitization of carbon black. J Appl Phys 25:1503–1509
18. Warren BE, Bodenstein P (1966) The shape of two-dimensional carbon black reflections. Acta Crystallogr 20:602–604
19. Treacy MMJ, Newsam JM, Deem MW (1991) A general recursion method for calculating diffracted intensities from crystals containing planar faults. Proc R Soc Lond A 433:499–520. http://www.public.asu.edu/~mtreacy/DIFFaX_manual.pdf
20. Egami T, Billinge SJL (2003) Underneath the Bragg peaks: structural analysis of complex materials. Pergamon Press Elsevier/Oxford University Press, Oxford
21. Scardi P, Ortolani M, Leoni M (2010) WPPM: microstructural analysis beyond the Rietveld method. Mater Sci Forum 651:155–171; Leoni M, Martinez-Garcia J, Scardi P (2010) Mater Sci Forum 651:173–186
22. Shull CG (1995) Early development of neutron scattering. Rev Mod Phys 67:753–757

23. Rietveld HM (1967) Line profiles of neutron powder-diffraction peaks for structure refinement. Acta Crystallogr 22:151–152
24. Rietveld HM (1969) A profile refinement method for nuclear and magnetic structures. J Appl Crystallogr 2:65–71
25. Young RA (ed) (1993) The Rietveld method. Oxford University Press/International Union of Crystallography, Oxford
26. Malmros G, Thomas JO (1977) Least-squares structure refinement based on profile analysis of powder film intensity data measured on an automatic microdensitometer. J Appl Crystallogr 10:7–11
27. Khattak CP, Cox DE (1977) Profile analysis of X-ray powder diffractometer data: structural refinement of La0.75Sr0.25CrO3. J Appl Crystallogr 10:405–411
28. David WIF, Shankland K, McCusker LB, Baerlocher C (eds) (2002) Structure determination from powder diffraction data. Oxford University Press, Oxford
29. Pecharsky V, Zavalij P (2008) Fundamentals of powder diffraction and structural characterization of materials. Springer, New York
30. Kisi EH, Howard CJ (2008) Applications of neutron powder diffraction. Oxford University Press, Oxford
31. Dinnebier RE, Billinge SJL (eds) (2008) Powder diffraction: theory and practice. RSC Publishing, Cambridge
32. Kroto HW, Heath JR, O’Brien SC, Curl RF, Smalley RE (1985) C60: buckminster-fullerene. Nature 318:162–163
33. Krätschmer W, Lowell D, Lamb D, Fostiropoulos K, Huffman DR (1990) Solid C60: a new form of carbon. Nature 347:354–358
34. Heiney PA, Fischer JE, McGhie AR, Romanow WJ, Denenstein AM, McCauley JP Jr, Smith AB III, Cox DE (1991) Orientational ordering transition in solid C60. Phys Rev Lett 66:2911–2914
35. Sachidanandam R, Harris AB (1991) Comment on ‘Orientational ordering transition in solid C60’. Phys Rev Lett 67:1467
36. David WIF, Ibberson RM, Matthewman JC, Prassides K, Dennis TJS, Hare JP, Kroto HW, Taylor R, Walton DRM (1991) Crystal structure and bonding of ordered C60. Nature 353:147–149
37. David WIF, Ibberson RM, Matsuo T (1993) High resolution neutron powder diffraction – a case study of the structure of C60. Proc R Soc Lond A Math Phys Eng Sci 442:129–146
38. David WIF, Ibberson RM (2012) in preparation
39. Coelho AA (2011) TOPAS academic; http://wwwtopas-academicnet/