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book reviews

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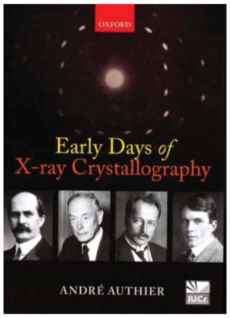

Early Days of X-ray Crystallography. By André Authier. International Union of Crystallography/Oxford University Press, 2013. Pp. xiv + 441. Price (hardcover) GBP 45.00. ISBN 978-0-19-965984-5.

> Laue in his talk to the Physikalische Gesellschaft in Berlin on 14 June 1912 showed the first picture obtained with copper sulphate, with a few odd spots, the audience cast a look full of attention and expectation at the image on the screen, but was not yet fully convinced. However when the first real Laue diagram appeared with its ordered diffraction points, an only feebly repressed *ah* went through the assembly. Everyone of us felt that a remarkable feat had been achieved, and that a hole had been pierced in an hitherto impenetrable wall.

So Max Planck stated 25 years later. Such detail as this is assembled in this remarkable book, impeccably researched by André Authier. This is perhaps an unusual way to start a book review, but I wondered how else to do justice to the topic and the quality of the book. To start with the one word 'Laue' also respects the nature of the transformation in crystallography in particular and science in general that that experiment brought. Today one often says 'Does the crystal diffract?' and follow that with 'Good, lets measure some photons'. X-ray wave–particle duality is now common to our daily language!

A reviewer of a book should not be daunted by the eminence of the author, but this is a challenge in this case. I hope my remarks below are then perceived as balanced. In any case, history leaves me some space to wriggle over interpretations of events, and also the clarity of the author's text allows me, just occasionally, to offer an alternate view. Of course as I am a mere youngster, entering my physics undergraduate degree in 1971, I did not meet Laue or Ewald or W. H. Bragg or W. L. Bragg. Instead, and because of their central roles through my career as a crystallography researcher and educator, I have steadily assembled their detailed writings, especially those of the Braggs, who wrote in English, my mother tongue. In the text below I refer to W. H. Bragg as WHB and W. L. Bragg as WLB. The book *50 Years of X-ray Diffraction*, edited by Ewald, and Ewald's own chapter therein are also a mine of information and viewpoints from the players of the time and the few decades after. I test what I read from other, secondary, sources of information with what these scientists themselves wrote. This is generally a sound approach, but of course some possible variation of their standpoints also has to be allowed for.

We can independently measure the impact of the critical initial period of X-ray crystallography (from approximately 1912 to 1914) from the book *Crystallography and Practical Crystal Measurement* by A. E. H. Tutton (1st Edition 1911, 2nd Edition 1922 in two volumes, 1446 pp.); Tutton was a Past President of the Mineralogical Society. I learnt of him from André Authier's book and purchased copies of the 2nd edition. Tutton wrote in his Preface to the Second Edition:

> The subject of Crystallography has made such remarkable progress since the year 1911, when the first edition of this book was sent to press, that a new edition is urgently called for. The startling discovery of Prof von Laue, that the planes of atoms in a crystal are capable of reflecting and diffracting X-rays, and thereby of revealing the inner structure of the crystal, was only made in Munich in the year 1912 . . . and the masterly development of this mode of attack on crystal structure by Profs. Sir W. H. Bragg and W. L. Bragg, together with the contributions of quite a number of other workers attracted to so novel a research, has rendered the last nine years a period of epoch making scientific progress . . . For a new light has been shed on crystallography . . . and the most satisfactory fact about it is that X-ray analysis has not only fully confirmed all the main conclusions as to crystal structure which were detailed in the first edition . . . crystalline substances occurring in 230 types . . . based on 14 space lattices . . . The atoms which we knew must be there, and in the positions we imagined, are now located in situ and their distances of separation determined in absolute measure.

The precise roles of Laue, WHB and WLB as described by Tutton have been of keen interest in the intervening decades up to the present day, and we follow these interests again below. André Authier says of his own book:

> The contributions of the main actors of the story, prior to the discovery [of X-ray crystallography], at the time of the discovery and immediately afterwards, are described [in this book] through their writings and are put into the context of the time, accompanied by brief biographical details . . . Numerous quotes from the writings of the main actors of the story tell how their discoveries were made and convey the spirit of their time.

It was Winston Churchill who reputedly said 'the farther backward you can look, the farther forward you are likely to see'. André Authier indeed takes us back much more than a hundred years. He also proposes (p. 129) a definition of ourselves as crystallographers. Paraphrasing only slightly:

> What is it that keeps the clan of crystallographers together? The inner structure of a material, ordered or not, its imperfections, at the nanoscopic, microscopic, or macroscopic scales, are directly related with its physical, chemical, mineralogical, or biological properties. The common goal of unravelling these structures or their defects by a large variety of techniques, and understanding their relations to the properties of materials, is what keeps the crystallographers together.

Thus, though you can grow the crystallographer out of physics or chemistry or biology, can you take the physicist, chemist or biologist out of the crystallographer? This is a well known and recurrent question. W. L. Bragg in both Manchester and Cambridge faced the question: Is crystallography proper physics? In Manchester, I know that the Physics Department here were proud enough of WLB to invite me to deliver the

W. L. Bragg Lecture on the occasion of the University's 150th Anniversary (available at http://www.iucr.org/education/teaching-resources/bragg-lecture-2001). We 'crystallographers as a clan', as André Authier calls us, need to be careful, though, as we are a science subject without undergraduate portfolio; there are courses in physics, chemistry, biochemistry *etc.*, but crystallography gets only crumbs of space within their crowded curricula. The national, regional and international crystallography bodies have here to take the firmest of roles in furthering crystallographic education of scientists from all disciplines if we are to allow crystallography to see far into the future, as per Churchill's statement above. André Authier's definition of our clan in his book stimulated much thought.

The relationship of WHB and WLB, father and son, is dealt with in one paragraph (pp. 145–146). The preoccupation of British, Australian and Canadian writers on this issue, with large sections of books given to it, is instead masterfully deferred by André Authier to the author of the Royal Society biography for WLB, Sir David Phillips, 'who knew him well, and worked closely with him' and who wrote in that biography that 'WLB's father, however hard he tried, did not quite avoid leaving the impression that his was the guiding part: what was no more than fair looked like parental generosity'. In my own readings, and leanings towards WLB, I became curious to learn more about WHB, stimulated especially by the book of John Jenkin. The X-ray spectrometer of WHB strikes me now as a remarkable piece of apparatus, as it is of course the forerunner of all X-ray diffractometers. The relative simplicity of crystal structure analysis with monochromatic reflection intensity data from the X-ray spectrometer gave it an incisiveness over Laue photography; moreover, the wavelength normalization and harmonics deconvolution in modern computer-based treatment of Laue intensity data was obviously not available to WLB. It is truly remarkable, therefore, that in WLB's analysis of the alkali halides he used Laue photographs, although the latter portion of WLB's pre-eminent June 1913 paper, hailed as 'the great breakthrough' by Ewald, did describe X-ray spectrometer measurements made by both WHB and WLB at Leeds. In that paper also, in a most ingenious way to my thinking, WLB obtained the unit cell using the size and volume of the crystal sample, its density and the mass of a hydrogen atom. This value then calibrated the wavelength of the X-ray tube of the X-ray spectrometer, which in turn enabled the determination of the unit cells of other crystal types. I would also add that the last paragraph of WLB's first paper of November 1912 (published in early 1913) suggests that WLB was planning his attack on the first crystal structure, where he would use an isomorphous pair or group of crystals; this research effort became to my mind his alkali-halides study, published in June 1913.

André Authier addresses the 'Forman controversy' within which the 'myth' is attacked that 'it could only have happened in Munich' (that X-ray diffraction could have been discovered). André Authier is quite diplomatic and even conciliatory about it, highlighting how certain details of Ewald and others had to be corrected. But to my younger-generation eyes, Munich's science and scientists of that time were a truly unique collection, with Roentgen, Groth, Sommerfeld, Laue and a certain PhD student Ewald! If WHB would have been recruited from Adelaide to Cambridge, instead of Leeds, thus joining the environment and legacy of Pope and Barlow, with their proposed face-centred cubic structure of alkali halides, along with WHB's experimental experience of X-rays, then maybe Cambridge could have had it all, X-ray diffraction and the first crystal structures. But Leeds recruited WHB, which yielded a development of the X-ray spectrometer apparatus. But who is to say what might have been. Apart from during the Great War and its aftermath, it seems in retrospect that the key players communicated well enough. So, to my eyes it was not a controversy. Indeed, as a measure of this apparent conviviality Laue was awarded an Honorary DSc from Manchester University in the mid-1930s, undoubtedly arranged by WLB, Professor of Physics there from 1919 to 1937. Likewise Laue, in his *Historical Introduction* to Volume I of *International Tables for X-ray Crystallography*, generously quotes WLB quite extensively.

I have given enough glimpses of the many jewels that this book contains to genuinely tempt the reader. I now need to convey some of the basic details. The book's contents are as follows:

1. Significance of the discovery of X-ray diffraction
2. The various approaches to the concept of space lattice
3. The dual nature of light
4. Röntgen and the discovery of X-rays
5. The nature of X-rays: waves or corpuscles?
6. 1912: The discovery of X-ray diffraction and the birth of X-ray analysis
7. 1913: The first steps
8. The route to crystal structure determination
9. X-rays as a branch of optics
10. Early applications of X-ray crystallography
11. Unravelling the mystery of crystals: the forerunners
12. The birth and rise of the space-lattice concept

A major interest and strength of the book are its many potted biographies about everyone you could ever wish to know about, creating a human face to each character that we know well: Miller (indices), Bravais (lattices), Weiss (crystal systems) and many more. In initially browsing the contents it struck me that Chapters 11 and 12 were better put at the beginning, and Chapter 10 after Chapter 8. In reading the book it becomes clear that the advantage of the order chosen by the author is to grip the reader early on; indeed, I never wanted to put the book down. That said, does one skip Chapters 11 and 12? Why no, for the reason Churchill gives that I quote above. Within Chapter 12, in fact, the logic of the order of chapters chosen by the author becomes clear. Within the summary of the centuries before 1912 to 1914 and Laue and the Braggs, we learn in detail the rich foundations of earlier work of crystallographers and mineralogists. In particular, as a sort of climax, Hauy 'hits upon, without realizing it, the structure of CaF_2 [Fig. 12.9, p. 327], more than a 100 years before Bragg'. In another such historical analysis it is shown that 'Wollaston in 1813 [see p. 336, Fig. 12.15 (diagram 14)] obtained a portion of the structure of a face-centred cubic binary compound such as sodium chloride, well before Barlow' in the late 19th century.

The readership of the book is given as 'Students and researchers in crystallography, chemistry, biochemistry, solid state physics, material science, and mineralogy. Also historians of science.' I concur with that list. Would a course lecturer on, say, structural chemistry or structural biology be able to recommend it for purchase? Additional reading yes, compulsory reading no.

What might be considered missing from *Early Days of X-ray Crystallography*? The nature of the uncertainty of the determination of atomic positions is an odd omission, not of the author but of accomplished physicists of the time. Ewald showed key essential steps involving the use of higher-order reflections in crystal structure analysis, *e.g.* of FeS_2; whereas WLB placed the sulfurs to one decimal place, Ewald determines them to three decimal places (p. 184). But the thorough treatment by Cruickshank of both chemical and later protein crystallography coordinate and vibration errors is not mentioned or referenced. This to me is a key point in our history: crystal structure analysis allows one to not only see atoms but also to know the precision of the method, and thereby deliver the various standard uncertainties of atomic positions and *B* factors. Crystal structure determination and the seminal work of Patterson (1934) on the F^2 synthesis and by Banerjee (1933) on the start of direct methods (http://www.iucr.org/publ/50yearsofxraydiffraction/full-text/banerjee) could also, I think, have been included in the story of the early stages of X-ray crystallography. The book's focus is obviously different from such further developments in crystal structure determination. The radically different nature of synchrotron radiation and the opportunities it presents could have been mentioned too, *e.g.* in Chapter 10, which includes DNA fibre diffraction, *i.e.* up to 1953.

In terms of production quality, Oxford University Press have made an attractive book-jacket front cover and further relevant books are listed on the inside back cover. The book uses high-quality paper. But, at around page 300, I found my eyes gave up struggling with the choice of a small typeface, also maybe exacerbated by the use of black type on a grey background for the biographical sketches of scientists. So, at this point, I bought my own e-book edition. This I found much better for my eyesight.

Are there any errors in the book? There are one or two wording errors but these are easily spotted. I had one critical benchmark: was the first crystal structure correctly given and described? The first X-ray crystal structure was sodium chloride, as is clear from WLB's own publications; there is no issue. This check has caught out other scientists in their writings and in radio broadcasts. I am glad to say that the start of Chapter 8 (p. 170) launches from the correct place, the crystal structure of sodium chloride. Page 148 does contain the sentence '...the exact structure of zinc blende [was] learned after reading Tutton's (1912*b*) letter to *Nature*'. The title of Tutton's article was *The crystal space-lattice revealed by Roentgen rays* and is quoted by the author in the reference list on p. 429. The use of the word 'structure' here instead of space-lattice and/or layout is obviously an innocent slip by the author, but it is important to be precise about the wording.

The reference list is extensive and immensely useful. It spans 33 pp. with approximately 40 references per page. A gem of a reference that I learnt about from this list is the collection of short articles entitled *Laue Diagrams, 25 Years of Research on X-ray Diffraction following the Prof. Max von Laue Discovery*, published in 1937 by the Indian Academy of Sciences in the journal *Current Science*. In these articles, the authors, who include most of the leading players of the time, summarise their views of developments since 1912. Another of my favourite references is missing though: W. L. Bragg's 1968 *Scientific American* article simply entitled *X-ray crystallography*. It is a cogent explanation for a wide audience. The reason for mentioning it here is that WLB states 'I first stated the diffraction condition ($n\lambda = 2d \sin \theta$) in this form in my initial adventure into research in a paper presented to the Cambridge Philosophical Society in 1912, and it has come to be known as Bragg's Law. It is, I have always felt, a cheaply earned honour because the principle had been well known for some time in the optics of visible light.' So, organisers of future X-ray Diffraction Centennial celebrations take note.

To sum up, one of the leading players in the modern era of X-ray crystallography, André Authier, has produced with this book a work of true devotion and incomparable detail. I found the book to be a captivating read. It should be studied by all with an interest in where we came from in our field of crystallographic science, and is a guide to where we are going.

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