Honouring the two Braggs: the first X-ray crystal structure and the first X-ray spectrometer

John R. Helliwell

To cite this article: John R. Helliwell (2013) Honouring the two Braggs: the first X-ray crystal structure and the first X-ray spectrometer, Crystallography Reviews, 19:3, 108-116, DOI: 10.1080/0889311X.2013.797410

To link to this article: http://dx.doi.org/10.1080/0889311X.2013.797410

Published online: 14 May 2013.

Article views: 1795

View related articles

Citing articles: 3

Download by: [T&F Internal Users], [Joshua Bayliss]  Date: 10 March 2017, At: 01:21
Honouring the two Braggs: the first X-ray crystal structure and the first X-ray spectrometer

John R. Helliwell*

School of Chemistry, University of Manchester, Manchester M13 9PL, UK

(Received 15 March 2013; final version received 16 April 2013)

In the Centennial celebrations of the birth of X-ray crystal structure analysis, a key feature is to mark the articles which are the first crystal structure analysis studies. This mini review describes the historical development and quotes key statements of W.L. Bragg (WLB) as well as W.H. Bragg (WHB) and the perspectives offered by key players of the time period. The first crystal layout, as stated by WLB, is the face-centred cubic arrangement evident in the Laue Laboratory diffraction photographs recorded from a crystal (of zinc blende) and provided to WHB. The first crystal structure, as stated by WLB, and explicitly remarked upon by P.P. Ewald, as well as WLB’s official biographer, D.C. Phillips, is sodium chloride and which was published in June 1913. The use of the X-ray spectrometer of WHB, and the measurements by WHB, at Leeds University, with this device are acknowledged by WLB in his article. This 1913 article also contains numerous raw diffraction data in the form of ‘Laue photographs’ measured by WLB of NaCl, and most importantly of KCl, in Cambridge. WLB seemed to anticipate the use of these two isomorphous and closely related alkali halide crystal structures in his article of 1912. The X-ray spectrometer as the forerunner of all X-ray diffractometer designs is also a remarkable initiative of WHB.

Keywords: first X-ray crystal layout; face-centred cubic layout; first X-ray crystal structure; sodium chloride; Laue diffraction photographs; the X-ray spectrometer

Contents

<table>
<thead>
<tr>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Introduction</td>
</tr>
<tr>
<td>2. The words of WLB</td>
</tr>
<tr>
<td>3. The words of WHB</td>
</tr>
<tr>
<td>4. The words of P.P. Ewald</td>
</tr>
<tr>
<td>5. The words of D.C. Phillips</td>
</tr>
<tr>
<td>6. Other perspectives</td>
</tr>
<tr>
<td>7. Conclusions</td>
</tr>
<tr>
<td>Notes on contributor</td>
</tr>
<tr>
<td>References</td>
</tr>
</tbody>
</table>

*Email: john.helliwell@manchester.ac.uk

© 2013 Taylor & Francis
1. Introduction
In the Centennial celebrations of the birth of X-ray crystal structure analysis, a key feature is to mark the article which is the first crystal structure analysis. This mini review describes the historical development and quotes key statements of WLB and the perspectives offered by key players of the time period.

2. The words of WLB
An excerpt from WLB’s first article in 1912 [1]:

It is only the third point system, the element of whose pattern has a molecule at each corner and one at the centre of each cube face, which will lend itself to the system of planes found to represent spots in the photograph (recorded by Messrs Friedrich and Knipping). This last system, seeing that it forms an arrangement of the closest possible packing, is according to the results of Pope and Barlow the most probable one for the cubic form of zinc sulphide.

Which of these factors it is that decides the form of the interference pattern might be found by experiments with crystals in which the point system formed by the centres of all the atoms differs from that formed by the centres of identical atoms.

In conclusion, I wish to thank Professor Pope for his kind help and advice on the subject of crystal structure.

These concluding words, ‘Which of these factors it is that decides the form of the interference pattern’, from WLB presciently explained the experiments that would lead to the first crystal structure.

From WLB’s words quoted by Ewald in [2]:

But let us hear in W.L. Bragg’s own words what the exciting sequence of events was after Laue’s paper had reached W.H. Bragg in (the) form of an offprint. He tells the story in an address given in 1942 in Cambridge at the first conference on X-ray analysis in industry (held under the auspices of the Institute of Physics), which was published in Science in Britain.

In order to examine the reflected X-ray beam (from a crystal face) more thoroughly, my father (William Henry Bragg (WHB)) built the X-ray spectrometer. The X-ray spectrometer opened up a new world. By using measurements made with the X-ray spectrometer, many of them due to my father, I was able to solve the structures of fluor spar, cuprite, zinc blende, iron pyrites, sodium nitrate and the calcite group of minerals. I had already solved KCl and NaCl, and my father had analysed diamond. Between them, these crystals illustrated most of the fundamental principles of the X-ray analysis of atomic patterns. These results were produced in a year of concentrated work, for the war in 1914 put an end to research. I have gone into these early experiments in some detail because it is a story which I alone can tell, and which I wish to put on record.

These reminiscences can be readily supplemented with the words of WLB in his book completed just two weeks before his death on 1 July 1971. Thus, from WLB (1975), The Development of X-Ray Analysis, p. 25 [3]:

I found that, although the range of wavelengths represented by the spots did not make sense if one assumed ZnS to be based on a simple cubic lattice everything fell into place if one assumed the basic lattice to be face-centred cubic. ... These results showed, not only that Laue’s pictures were made by a continuous range of X-ray wavelengths, a kind of ‘white’ radiation, but also that X-ray diffraction could be used to get information about the nature of the crystal pattern.
The next text page 27 [3] begins with the heading which is Section 5 in Chapter 2 of ref 3 in turn headed “THE START OF X-RAY ANALYSIS” and then quotes the last paragraph of this section on page 30.

Page 30 [3]:

The First Complete Analyses: The Alkali Halides
It was on this rather indirect and slender evidence that I assigned the structure of Fig 12 (see Figure 1) to the alkaline halides in a paper read to The Royal Society in June 1913 [4]; fortunately further investigation established its correctness! These were the first crystals to be analysed by X-rays. As the structure was now established, it was possible to calculate dimensions from the crystal density and the mass of the NaCl molecule. Half a molecule is associated with each small cube of side \( a = AB \) in Fig 12 (Figure 1) so

\[ \frac{1}{2}Mm = \rho a^3, \]

where \( M \) is the molecular weight, \( m \) is the mass of the hydrogen atom, and \( \rho \) is the density of the crystal. This gave a value for \( a \) of \( 2.8 \times 10^{-8} \) cm and so established a scale for the measurement of all X-ray wavelengths and crystal spacings.

There is now a Chapter devoted to the first crystal structure analysis:-

Page 53 [3]:

Chapter 5 THE FIRST ANALYSIS OF CRYSTAL STRUCTURE

The Method of Analysis

Although the NaCl structure was deduced from Laue photographs, the first results with the X-ray spectrometer showed at once how far more powerful it was as an analytical tool. When I started work in the Leeds laboratory in the summer of 1913, my father was still mainly interested in exploring the X-ray spectra. It fell to me to use the spectrometer [5] for determinations of crystalline arrangement and a number of inorganic structures were discovered. We wrote a joint paper on diamond [6] and the other structures were described in a paper in The Royal Society Proceedings in 1913 which may be said to represent the start of X-ray crystallography.
It was very fortunate for me that I was able to work in my father’s laboratory. Young research students nowadays can have little conception of the primitive conditions in a research laboratory some sixty years ago. (However) In my father’s laboratory … at Leeds there was a good workshop with an excellent mechanic in charge to carry out his ideas. It was the privilege of working with really effective apparatus which made it possible for me to start my research career by working out a number of crystal structures. … The analysis depended on comparing the strength of the various orders of reflection. When the planes are identical and evenly spaced the orders fell off regularly… A marked departure from this regular diminution indicated that the planes were not simple. … The (crystal structures analysed) included fluor spar, zinc blende, pyrites and calcite (in various forms).

3. The words of WHB

WHB’s own words, extracted from the article [7] of his son’s role (see Figure 2):

From the work now described by W L Bragg it appears that the reflection phenomena lead to a more definite knowledge of crystal structure, and we may now complete various quantitative determinations. … (namely) the (X-ray) wavelengths of various homogeneous rays as soon as their angles of reflection are known (from an NaCl or other single crystal).

[The unit cell parameter for the cubic NaCl having been established ingeniously from the mass of a crystal, its volume and the atomic weights of sodium and chlorine, as described above.]

The X-ray spectrometer was also noted by WHB to be under similar development and use at Liverpool University by Barkla and at Manchester University by Moseley and Darwin; for a summary description see [8].

4. The words of P.P. Ewald

Page 65 of ‘Fifty Years of X-ray Diffraction [2]’:

Although this early paper (WLB 1912 [1]) does not yet contain a full structure determination, it comes very close to one, in the case of such a simple compound as ZnS.

Page 69:

The great break-through to actual crystal structure determination and to the absolute measurement of X-ray wavelengths occurred in W L Bragg’s (NaCl) paper [4].

Page 71:

In the series of fundamental papers published by both Braggs in 1913 and 1914 this paper by W L Bragg unquestionably brings the greatest single advance … … it made all future structure determinations very much easier by providing an absolute wave-length scale … It would, however, be an invi
dious undertaking to single out any one of the early papers as the most important one, so closely were they all interlinked and so rapid was the progress at the time of their writing which formed a back
ground for their formulation.

Page 72:

The joint paper The Structure of Diamond [6]:

was the first example of a structure in which the effective scattering centres did not coincide with the points of a simple (Bravais type) lattice. The determination of this structure was acclaimed as a great triumph of the new methods. Whereas in the structures of rock salt, zinc blende and fluorite the absence of molecules in the accepted sense created an element of bewilderm ent, the beautiful confirm
ation of the tetravalency of carbon on purely optical principles made this structure and the method by which it was obtained immediately acceptable to physicists and chemists alike.
The Reflection of X-rays by Crystals. (II.)

By W. H. Bragg, M.A., F.R.S., Cavendish Professor of Physics in the University of Leeds.

(Received June 21,—Read June 26, 1913.

This note is a supplement to a paper on the reflection of X-rays by crystals which has been recently communicated to the Royal Society.* It is there shown that the wave-length of a homogeneous beam of X-rays can be found accurately in terms of the spacing of the elements of a crystal. There has been some doubt as to the actual arrangement of the atoms in the crystal and in consequence it was not possible in the paper quoted to draw any final conclusions as to wave-length values. From the work now described by W. L. Bragg it appears that the reflection phenomena lead to a more definite knowledge of crystal structure, and we may now complete various quantitative determinations.

The elementary volume in rock-salt is a cube with 1 atom of sodium at each of four corners and 1 atom of chlorine at each of the other four. In other words the number of elementary volumes in any space of measurable dimensions is equal to the number of atoms in that space.

The number of molecules in 1 c.c. of NaCl is

\[
\frac{215}{58.5} \times 1.64 \times 10^{-21} = 2.24 \times 10^{22}
\]

(The weight of the H atom is taken to be 1.64 \times 10^{-21}.)

The number of atoms is twice as great and the elementary cube volume is therefore \(1/4.48 \times 10^{22} = 2.23 \times 10^{-21}\). The edge of the cube is 2.81 \times 10^{-8}; this is the distance between consecutive reflecting planes parallel to (100).

The principal bundle of homogeneous X-rays from a platinum anticathode is stated in the paper quoted to be reflected at the (100) face of rock-salt at a glancing angle of 11.55°. Recent observations with better apparatus show that this bundle is really double, consisting of two separate sets whose wave-lengths differ from each other by a little less than 2 per cent. of either; they also show that the first estimate was a little too high. For the purpose of the present argument it is sufficiently accurate to ignore the division and assume the angle to be 11.3°. This gives a wave-length

\[
(2d \sin \theta) = 2 \times 2.81 \times 10^{-8} \times 0.196 = 1.10 \times 10^{-8}
\]

The wave-lengths of other homogeneous rays can then be found easily as soon as their angles of reflection are known.


Figure 2. From [7]. Further text extracts of the various papers from WLB and/or WHB are in the centennial celebration article [8].
The paper The Analysis of Crystals with the X-ray Spectrometer [9] shows remarkable progress in a number of ways … (this included the fact that) it is clearly recognized that for a complete structure analysis the intensities of the reflections have to be known and evaluated.

5. The words of D.C. Phillips

David Phillips, who knew WLB directly, e.g. at The Royal Institution, wrote the Biographical Memoir of WLB in The Royal Society series [10]. On pages 88–89 referring to WLB 1912 he states

The critical test was to see whether these ideas (of WLB) explained the observations from (the) ZnS (Laue diffraction photographs), including the absence of some spots predicted by Laue’s analysis. Here (W L) Bragg inverted the argument and used the fact that the X-ray pulses can be regarded to be a ‘white light’ spectrum extending over a characteristic range of wavelengths and with maximum energy at certain wavelengths. The intensities of the Laue spots ought, therefore, to fall in a regular series depending upon which part of the spectrum was responsible for each of them. Examinations showed that this did not work … (W L) Bragg tried to explain the ZnS pattern (of diffraction spots) on the assumption that the structure is face-centred cubic and everything fell into place. Thus he showed that the Laue pictures were made by a continuous range of X-ray wavelengths … and that X-ray diffraction could be used to get information about the crystal structure. This was the start of the X-ray analysis of crystals … The next papers were published at about the same time (June 1913). In the first of them WHB derived the wavelengths of various radiations and correlated them with Barkla’s characteristic radiations, making use of the structure of rock salt which had been worked out by his son, but not yet published. This paper was immediately followed by Bragg’s detailed account [4] of NaCl and related structures described by Ewald [2] as ‘the great breakthrough to actual crystal structure determination and to the absolute measurement of X-ray wavelengths’. The analysis depended mainly on Laue photographs taken in Cambridge, supported by some measurements with the (WHB) spectrometer.

6. Other perspectives

The Royal Society Obituary Notice for WHB was written by Andrade and Lonsdale [11]. It contains a synoptic paragraph of their achievements (Figure 3). The emphasis given in [11] between WLB and WHB, son and father, in that synopsis seems not to be correct not least with respect to WHB’s own words of his son’s work (see above) from [7].

The work of Bragg and his son Lawrence in the two years 1913, 1914 founded a new branch of science of the greatest importance and significance, the analysis of crystal structure by means of X-rays. If the fundamental discovery of the wave aspect of X-rays, as evidenced by their diffraction in crystals, was due to Laue and his collaborators, it is equally true that the use of X-rays as an instrument for the systematic revelation of the way in which crystals are built was entirely due to the Braggs. This was recognized by the award of the Nobel prize for Physics in 1915 to them jointly ‘pour leurs recherches sur les structures des cristaux au moyen des rayons de Roentgen’, and a further formal acknowledgment was the appearance in Leipzig, in 1928, of a collected reprint, in German translation, of the early papers, under the title Die Reflexion von Röntgenstrahlen an Kristallen: grundlegende Untersuchungen in den Jahren 1913 und 1914 von W. H. Bragg und W. L. Bragg.

Figure 3. Text extract from [11] by Andrade and Lonsdale.
This perhaps explains the modern comment of the type:

11 November 2012 marks the centenary of the reading of the paper by William Lawrence Bragg (WLB) to the Cambridge Philosophical Society outlining the foundations of X-ray crystallography. It included the derivation of the first correct atomic structure of a crystal, namely that of zinc blende, based on the X-ray diffraction pattern recorded by Friedrich, Knipping and Laue in the spring of 1912.

This comment can be read recently: in Acta Cryst Section A and in at least two newsletters of national crystallographic societies or listened to on the radio by scientific commentators.

Perhaps most remarkably, the following appeared in the paperwork for the IUCr Madrid Congress of the Crystallography General Assembly papers opening the item on the International Year of Crystallography (note now to be held in 2014 not 2013):

In 1912 Max Laue showed that X-rays were diffracted by crystals and W.L. (Lawrence) Bragg presented a paper to the Cambridge Philosophical Society both presenting Bragg’s Law and the correct structure of zinc blende, which he derived from the X-ray diffraction data obtained from Laue. W.H. and W.L. Bragg rapidly carried out a number of key diffraction experiments of their own that led to the determination of crystal structures that were published in 1913. These ground breaking experiments mark the birth of modern crystallography. The International Union of Crystallography (IUCr) is marking the centennial of these events by declaring 2013 the International Year of Crystallography (IYCr2013).

If the substance of the modern comments highlighted just above were to restrict themselves to the layout of a crystal, it would be factually correct, namely face-centred cubic in the case of WLB’s 1912 analysis [1]. Those modern recent comments however, arguably much more important, also seem to basically ignore the importance of the X-ray spectrometer and the monochromatic X-ray measurements from the crystals that it empowers. The Laue method of white X-rays, as WLB pointedly remarks [1], is very sensitive to the crystal orientation, whereby the intensities of individual reflections are altered. Of course the systematically absent reflections have zero intensity whatever the crystal orientation and which is why the Laue method was adequate for WLB to use it to determine the face-centred cubic lattice layout from the diffraction photographs [1] provided by Laue to WHB. Indeed the wavelength normalization of the Laue photographic intensities has been a key step of the modern synchrotron Laue method of complete quantitative crystal structure analyses [12]. Again, as WLB remarks, the move towards more complicated crystal structures, like diamond, in 1913 into 1914 was firmly implanted within the use by WLB, along with his father, of the X-ray spectrometer.

Further extensive documentation of the achievements of WLB is available in the volume by Thomas and Phillips [13] and the Special Issue of Acta Crystallographica Section A: Foundations of Crystallography January 2013 [14]. A tribute to the work in X-ray analysis of WHB is the scientific summary written by North [15]. A further, recent, tribute to the work of WLB is given by Thomas [16] and from which I quote 1913 marks the year when X-ray crystallography, through the determination of the structures of sodium chloride, potassium chloride, potassium bromide and potassium iodide and of diamond first made its striking impact.

7. Conclusions

This Historical Note honours the first crystal structure, that of WLB’s NaCl, published in June 1913 [4]. The earlier, also truly remarkable, analysis by WLB of the face-centred cubic layout of a crystal from the pattern of systematic absences in the Laue diffraction photographs of ZnS [1], included WLB’s anticipation in his concluding paragraph of what studies and experiments he would have to make to determine the first crystal structure, i.e. with the placement of the
Na and Cl atoms [4]. The prompt subsequent development of the X-ray spectrometer apparatus by WHB in Leeds [5], and its use by his son and by himself, led to the more quantitative analysis of the monochromatic X-ray measurements from single crystals. The first X-ray crystal structure, that of NaCl, described vividly in WLB’s own words [2,3] is a truly absorbing, wondrous, iconic story in the History of Crystallography and indeed of all of science. The critical nature of the contribution of a new piece of apparatus, the X-ray spectrometer [5], and the measurements it empowered in these studies is also a wondrous development.

Notes on contributor

John R. Helliwell trained as a physicist (York University, 1st class Hons degree) and then a protein crystallographer (DPhil., Oxon). He spent the first 20 years of his research career, from 1979, walking in the footsteps of William Henry Bragg with the design and build of the Daresbury Synchrotron Radiation Source Station 7.2 tuneable synchrotron X-ray spectrometer for protein crystallography. This synchrotron radiation X-ray spectrometer was followed by SRS wiggler Station 9.6, also tuneable, but extended to shorter X-ray wavelengths, then SRS wiggler Station 9.5 which was rapidly tuneable, and finally the rapidly tuneable and high X-ray intensity of the instrument ESRF BM14 (this latter project led by Andrew Thompson). In the last 20 years, JRH switched emphasis and followed in the footsteps of William Lawrence Bragg, based at the University of Manchester from 1989 as Professor of Structural Chemistry, and where he has undertaken a wide variety of crystal structure analyses of proteins and nucleic acids, using X-rays and more recently with neutrons. He is now an Emeritus Professor at the University of Manchester.

References

Subject Index

Crystal structures of
  - diamond 2, 3, 7, 8
  - NaCl 1–5
Face-centred cubic lattice 1, 2, 5, 7
Laue diffraction photographs 5, 7, 8
Systematically absent X-ray intensities 7
X-ray spectrometer 2–5, 7, 8
X-ray wavelengths 2, 3, 5, 8