Invited Comment

Crystallography and physics

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Abstract

X-ray crystallography was initiated by physicists in the early 20th century. However—as is common with many developments in physics—the subject quickly moved beyond the confines of physics to produce key advances in chemistry, biology, mineralogy and materials science. This article discusses the role of physics in developing crystallography over the last 100 years and the relevance of crystallography to physics today. It is concluded that although crystallography has become somewhat hidden within physics departments it is still a key component of modern condensed matter physics.

Keywords: crystallography, x-ray diffraction, history

1. Introduction

In 1912 physicist Max Laue [1] discovered that crystals would diffract x-rays and physicist Lawrence Bragg used this discovery to derive Bragg’s Law [2] and together with his father William—also a physicist—established the field of x-ray crystallography [3, 4]. The first crystal structure solved using these methods was that of rocksalt (NaCl) in 1913 [3] and 1914 and 1915 saw the Nobel Prizes in Physics awarded to von Laue [3] and the Bragg father and son team, respectively [5].

Since 1912 the field of crystallography has developed enormously and now directly and indirectly influences all aspects of our lives through its contributions within physics, chemistry, materials science and biology. The subject’s importance is demonstrated by the many Nobel Prizes that have been awarded to those working within crystallography [6] although the majority are given in chemistry and often to those working on biological systems. The 2009 Nobel Prize in Chemistry awarded to Venki Ramakrishnan, Thomas Steitz and Ada Yonath ‘for studies of the structure and function of the ribosome’ [7] is a good example of this. Interestingly, and in common with many other crystallographers working across varied disciplines, Venki Ramakrishnan initially trained as a physicist, obtaining a PhD in physics from Ohio University. This observation may indicate that physics and crystallography are more strongly dependent on each other than is often acknowledged. It is this relationship that this article aims to explore.

2. The contributions of physics—and physicists—to crystallography

The initial discovery that crystals will diffract x-rays came from within one of the pre-eminent physics laboratories in Europe, when Max Laue was working in Arnold Sommerfeld’s Institute for Theoretical Physics in Ludwig-Maximilians-Universität in Munich. (The measurements were prompted by a discussion with Peter Paul Ewald, a physicist who went on to develop many key crystallographic principles and was instrumental in the organization of the worldwide crystallographic community through the formation of the International Union of Crystallography and the Acta Crystallographica journal.) The scientific discipline of x-ray crystallography emerged within a year or two of Laue’s discovery through Lawrence Bragg’s early developments of the theory to relate x-ray diffraction to crystal structure [3] and

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William Bragg’s rapid improvements to x-ray instrumentation for crystallographic studies [8]. Lawrence later said of these early years with his father’s x-ray spectrometer,

‘It was a glorious time, when we worked far into every night with new worlds unfolding before us in the silent laboratory’ [9] (p 62) and, ‘It was like discovering an alluvial gold field with nuggets lying all round waiting to be picked up’. [9] (p 224)

To place this momentous turning point in context, prior to Laue’s discovery in 1912 crystallographers were only able to study the macroscopic properties of crystals (size, shape, symmetry, etc); atomic structure was only conjectured. Nonetheless a number of principles governing crystal symmetry had slowly been established (see [10, 11]) by an eclectic mix of mineralogists, physicists, mathematicians and priests: in the 18th century, French priest René Just Haüy noticed that crystals cleaved into smaller crystals of specific form or ‘habit’ suggesting that they were composed of stacked repeating blocks; in 1830, mineralogist Johann Hessel derived the 32 possible crystal classes based on external crystal morphology—later identified as the 32 crystallographic point groups of lattice symmetry; physicist Auguste Bravais identified his 14 distinct eponymous lattices in 1848; the 230 space groups were derived independently by mathematicians Evgraf Fyodorov and Arthur Schoenflies in 1890 and 1891, respectively and by gentleman scientist William Barlow in 1894; and the concept of \((hkl)\) ‘Miller’ indices to describe crystal faces was introduced by mineralogist William Miller in 1839—later used to ‘label’ Bragg reflections. Developments of the crystallographic method were far more rapid post 1912; indeed it is remarkable how quickly the essential theories of x-ray crystallography became established (see a discussion by Lawrence Bragg [9], chapter 8, p 120), largely through the work of physicists. In a series of papers Charles Galton Darwin, Arthur Compton and others developed formulæ for quantitative calculation of x-ray intensities in terms of electromagnetic theory and incorporating effects of thermal motion [19]; Douglas Hartree calculated the atomic form factors [18] and Peter Debye calculated the effect of thermal motion [19]—further developed by Ivar Waller [20]—to give the Debye–Waller factor. Crystal structure solution methods using diffraction data quickly increased in sophistication (see [21] for a good summary): the Bragg developed methods of Fourier analysis in one and two dimensions (e.g. Lawrence Bragg’s work on diopside [22]); Arthur Patterson extended this to three dimensions [23] in the 1930s; so-called ‘direct methods’ followed in the years after the Second World War (for which mathematician Herbert Hauptman and chemist Jerome Karle received the Nobel Prize in Chemistry in 1985) [24, 25]; and these contributed towards the developments of multi-wavelength anomalous diffraction (MAD) and single-wavelength anomalous diffraction (SAD) techniques that are routinely used to determine protein structures from x-ray diffraction today.

Most developments in instrumentation and sources that led to improvements in the crystallographic technique were initiated by physicists. William Bragg’s two circle diffractometer design with an ionization chamber detector was a significant improvement on the photographic film methods of Laue, Paul Friedrich and Walter Knipping [1] as it allowed the separation of Bragg reflections arising from different x-ray wavelengths and the measurement of absolute Bragg peak intensities. The downside of this approach was that it took a long time to collect significant quantities of data. Photographic methods were therefore still used to survey the scattering in reciprocal space using methods that separated the Bragg reflections in a convenient manner. These advanced rotating crystal methods were exemplified by the Weissenberg [26] and precession [27] cameras where the photographic film was also moved in tune with the crystal rotation (the latter providing an undistorted picture of the reciprocal lattice) and could be used to determine the crystal unit cell, index the Bragg reflections and identify the crystal symmetry [28]. Photometric measurements of the Bragg spots could be used to estimate intensities, although this was never as precise as the intensities obtained when using x-ray detectors [28].

Most modern single crystal diffractometers are based on a combination of William Bragg’s spectrometer and the photographic film techniques developed after the First World War, albeit with vastly improved detectors, monochromatic x-ray sources, optics and mechanics.

In powder diffraction all early x-ray diffractometers were developed by physicists, beginning with the Debye–Scherrer camera [29] in 1916 (and another similar design by Albert Hull a year later [30]) for samples loaded into glass capillaries and later improved by André Guinier [31] through monochromatizing and focussing the incident x-ray beam to produce the Guinier camera. Optimization of the geometry for powder diffraction with divergent beams and flat plate samples was achieved by Johannes Brentano, in collaboration with Lawrence Bragg. Electron diffraction was demonstrated in the 1920s by physicists George Thomson, Clinton Davisson and Lester Germer; Thomson and Davisson went on to receive the Nobel Prize in Physics in 1937 for the discovery of the diffraction of electrons by crystals [32]. Neutron diffraction was initiated by physicists Ernest Wollan and Clifford Shull while working at Oak Ridge National Laboratory; the latter received the Nobel Prize in Physics in 1994 with Bertram Brockhouse for the development of the neutron scattering technique, 10 years after the death of Wollan and nearly 50 years after their pioneering work. Their experiments were instrumental in showing how neutron diffraction can be used to locate hydrogen atoms in crystal structures and to determine the magnetic structure of materials. It is a similar story with x-ray and neutron sources; developments of x-ray tubes, synchrotrons and neutron-producing reactors and spallation sources all relied on substantial input from physicists. Physicist Wilhelm Röntgen discovered x-rays [33] using Crookes-Hittorf vacuum tubes and these were used by early x-ray crystallographers until the development of tubes with hot-filament cathodes and better vacuums. The theory behind synchrotron radiation was developed by Alfred-Marie Liénard and Emil Wiechart at the turn of the 20th century, before being observed...
experimentally by physicists and engineers in the 1940s. This ‘nuisance’ radiation was later harnessed for x-ray crystallography and other x-ray scattering experiments leading to modern x-ray synchrotron facilities [34] of which there are over 40 worldwide [35]. Physicist John Madey developed the free electron laser (FEL) in the 1970s [36], a forerunner of x-ray FELs, the first of which became operational in Stanford, California in 2009. These XFELs now produce extremely intense beams with wavelengths suitable for crystallography applications.

3. The impact of crystallography on physics

Kathleen Lonsdale wrote in 1962 [9], p 221ff:

“The early workers in the field of x-ray diffraction were not at first interested in the physics of crystals as such but in the fundamental problems of physics itself: properties of matter, heat, light, sound, electricity and magnetism. Crystals and the diffraction of x-rays by crystals were simply tools with which to investigate such phenomena as cohesion, rigidity, elasticity, changes of state, expansion, the nature and properties of radiation and its interaction with matter.’

She then proceeded to outline how crystallography:

(i) has determined ionic and atomic radii—changes to structures under pressure has led to an understanding of fundamental bonding behaviour;
(ii) has characterized ferroelectricity, dielectric behaviour and piezoelectricity at an atomic level—‘communication, entertainment, adult education and propaganda have been almost entirely transformed during the past forty years because of this single development of an obscure and somewhat mysterious crystal property’ [9], p 242;
(iii) has shown how structure impacts on the behaviour of metals, including texture, defects and alloying;
(iv) has made a major contribution to crystal dynamics—thermal expansion, vibration, elastic constants, specific heat, thermal conductivity and superionicity;
(v) has allowed the interpretation of magnetic behaviour in terms of magnetic structure; and
(vi) has provided an atomic-level understanding of the optical properties of crystal—polarizations, left- and right-handedness, birefringence.

This is a fairly substantial list, and it was written over 50 years ago!

If we look at condensed matter physics today, we immediately see that whole swathes of physics research are dependent on crystallography. Superconductivity requires a knowledge of crystal structure, as do the fields of multiferroics, exotic and low-dimensional magnetism, quantum materials and phase transitions, correlated electron systems, and areas of optoelectronics and semiconductor physics. Indeed, as appreciated by Neumann in the 19th Century [37], any study where the physical phenomenon is supported by a crystal structure is explicitly dependent on crystallography. Crystallographic principles are also implicitly assumed in many theoretical studies; quantum mechanical models of electronic band structure in solids assume a knowledge of structural periodicity and where the atoms are (e.g. the ‘muffin-tin’ approximation) as do calculations that use density functional theory with Bloch wavefunctions.

Other areas of physics research are perhaps only on the fringes of ‘traditional’ crystallography, but these are very much areas where there are active developments in crystallographic methods and theory. These include studies of applied physics using thin-film technologies (spintronics, photovoltaic cells, etc), and applications using nanocrystalline materials. The latter is benefitting from very effective recent developments of so-called ‘pair-distribution function’ methods [38], initially developed by physicist Bertram Warren in the early days of x-ray diffraction for studying amorphous materials [39] and from recent experiments using coherent x-ray diffraction imaging [40].

4. Perceptions of crystallography within physics

Laue’s discovery of x-ray diffraction has had far wider implications than ‘merely’ establishing x-ray crystallography. Albert Einstein promptly wrote to congratulate him, ‘Dear Mr Laue! I cordially salute you on your wonderful success. Your experiment counts among the most glorious that physics has seen’ [41]. And this sentiment has stood the test of time; in a comment article written 100 years later it was described as ‘the amazing turning point’ and ‘a central event’ in modern science [42]. X-ray diffraction was not only able to show the arrangements of atoms in crystals, but by determining the wavelengths of x-rays, crystals could be used to study the nature of the atom itself. Despite this, the same centennial article [42] asks why this discovery has been given a relatively minor place in the history of physics, while noting that condensed matter physics is often seen as less prestigious than other areas of physics.

In John Jenkins’s biography of William and Lawrence Bragg [43] there is a considerable discussion of the interplay between the Braggs and the physics community in which they worked. Both held senior professorial chairs in physics departments: William in Adelaide, Leeds and University College London; Lawrence was head of the physics department in Manchester and of the Cavendish Laboratory in Cambridge, succeeding Ernest Rutherford in both cases. Yet it appeared necessary—particularly for Lawrence Bragg—to justify their physics credentials. Lawrence Bragg wrote to Rutherford in 1929, when he was thinking about possibly returning to Cambridge,

‘I do not want to label myself a crystallographer as against a physicist and think indeed that though my research is concerned
with crystals it is the physical side of it which attracts me.’ And, ‘...subject of crystallography by itself is very limited. The parts of it which are growing and important are really pure physics, and it would best be developed as part of a big Physics School, not as a subject on its own.’ [44]

Modern readers may view these statements as part of a pitch for a key position in physics and thus perhaps overstating the argument, but the desire for his research to sit comfortably within the physics mainstream was clear: ‘I always wish I were in a field which had more right to be called Physics’, he confessed to his close colleague, Harold Robinson [43]. So he would have been pleased with this statement in his obituary:

‘He (Lawrence Bragg) never lost sight of the fact that he was a physicist. He placed physical insight and understanding before theoretical manipulation. He was always concerned with the basic physical principles behind the work that he was doing, when so many other people were content just to use the formulae that he and others had developed.’ [45]

When Lawrence Bragg did become Cavendish Professor of Experimental Physics in 1938, one year after the death of Rutherford, there was some disquiet as many hoped that another nuclear physicist might be appointed [44] (p 110). Bragg also initiated organizational changes, establishing a structure composed of a number of more autonomous and diverse research groups. Although disruptive at the time, they came to be seen positively, as Brian Pippard remarked much later in 1972:

‘Bragg performed a notably excellent job in decentralizing the work of the Cavendish, and thus effectively breaking away from what would have ultimately become the dead hand of the Rutherford tradition. His decision to give each research section as near as possible autonomy, consistent only with very general central principles and of course financial control, has played a significant part in the subsequent developments.’ [44] (p 117)

However crystallographic work, sometimes after initial skepticism, was receiving considerable acceptance in other disciplines. In chemistry, one early skeptical response was vitriolic. The following, under a title ‘Poor Common Salt!’ was a rapid response to a lecture given by Lawrence Bragg at the Royal Institution (and subsequently reported in Nature in 1927) [46]:

“Some books are lies frae end to end,” says Burns. Scientific [...] speculation would seem to be on the way to this state! [...] on p 414 [of Nature, Sept 17], Prof. W L Bragg asserts that “In sodium chloride there appear to be no molecules represented by NaCl. The equality in number of sodium and chlorine atoms is arrived at by a chess-board pattern of these atoms; it is a result of geometry and not of a pairing-off of the atoms.”

This statement is more than “repugnant to common sense.” It is absurd to the n...th degree, not chemical cricket. Chemistry is neither chess nor geometry, whatever x-ray physics may be. Such unjustified aspersion of the molecular character of our most necessary condiment must not be allowed any longer to pass unchallenged. A little study of the Apostle Paul may be recommended to Prof. Bragg, as a necessary preliminary even to x-ray work, especially as the doctrine has been insistently advocated at the present Flat Races at Leeds, that science is the pursuit of truth. It were time that chemists took charge of chemistry once more and protected neophytes against the worship of false gods: at least taught them to ask for something more than chess-board evidence.’ [47]

Admittedly this attitude was probably more the exception, and certainly when Lonsdale, who at the time was working in the Physics Department in Leeds, presented x-ray diffraction evidence from hexamethylbenzene in 1929 [48] and two years later from hexachlorobenzene [49] for a flat hexagonal benzene ring, it was greeted much more positively. Christopher Ingold, a Professor of Chemistry in Leeds, wrote in 1931:

‘Ever so many thanks for the reprint of your wonderful paper on Hexachlorobenzene. [...] The calculations must have been dreadful but one paper like this brings more certainty into organic chemistry than generations of activity by us professionals.’ [9] (p 600)

Crystallography also rapidly extended into biology [21] with a diversification of the scientific backgrounds of the crystallographers. Work on fibre diffraction by physicist William Astbury in the 1930s led to the discovery in 1953 of the double-helical structure of DNA by James Watson (who initially studied zoology) and physicists Francis Crick and Maurice Wilkins, using chemist Rosalind Franklin’s x-ray diffraction photographs of DNA fibres. A band of Nobel-prize-winning chemists worked on the emerging field of macromolecular crystallography: Dorothy Hodgkin solving the structures of penicillin and the larger molecule vitamin B_{12} in the 1940s and 1950s; John Kendrew and co-workers determined the structure of myoglobin; and Max Perutz of hemoglobin in the 1960s. Biological crystallography in its infancy was nurtured within the physics department in Cambridge without any difficulties associated with this apparent contradiction. On arrival in Cambridge, Lawrence Bragg encouraged this work—began under the direction of John Desmond Bernal some ten years earlier—by enabling...
Perutz to remain at the Cavendish ([44], pp 110–1) and later in 1947 by persuading the Medical Research Council to support a Unit for Research on the Molecular Structure of Biological Systems, famously housed in a ‘hut’ within the Cavendish. This highly successful venture became the world-renowned MRC Laboratory of Molecular Biology, collecting a number of Nobel Prizes along the way.

Jenkin discusses the subsequent demise of crystallography in the Cavendish on Bragg’s retirement in 1953 ([43], p 437). Nevill Mott, Bragg’s successor, made it clear that he did not intend to keep the MRC Unit in his department and it moved into its own buildings elsewhere in Cambridge in 1962 [50]. Although this led Jenkin to assert, ‘In its premier British home, physics had finally cast out x-ray crystallography’ the situation was probably a little more nuanced than this. The MRC Unit by this time was seeing significant results and 1962 coincided with the Nobel prizes to Perutz and Kendrew and to Crick, Watson and Wilkins; with the exception of Wilkins, all were working at the Unit at the time and the Unit had clearly outgrown its Cavendish home. However, crystallographers remained in the Cavendish into the 1970s. Around this time there were several retirements, including Helen Megaw in 1972, Jane Brown moved to the Institut Laue-Langevin in 1974, and when Mike Glazer left for Oxford in 1976 he was indeed the last x-ray crystallographer in the department, albeit 22 years after the arrival of Mott and five years after his retirement from the Cavendish Chair [51].

There is however little doubt that crystallography has low ‘visibility’ in physics departments today and this is largely due to ‘labelling’. Like Lawrence Bragg, few physicists will choose to be labelled a ‘crystallographer’ above a ‘physicist’, and few groups in physics whose research is strongly crystallographic headline their work as ‘crystallography’ on departmental web-sites; they are the ‘structural condensed matter physics group’ or ‘nanoscale physics group’ or ‘materials physics group’ or some such similar wording. They also do not tend to embrace the wider crystallographic community; a search on physics in the World Directory of Crystallographers returns only 211 matches, or less than 2% of the many thousands of entries [52]. Also, since the 1970s, there has been a growth in central research facilities based around neutron scattering and x-ray synchrotrons (and more latterly, FELs). Jane Brown left the Cavendish for the Institut Laue-Langevin, the same year that the UK formally joined France and Germany as its third Associate Member. Many other physicists who work as crystallographers have taken a similar path and are employed in national and international laboratories. This is because these laboratories are seen to be where the technical advances in diffraction physics and crystallographic instrumentation are occuring and therefore where physical crystallographers naturally congregate. Of course crystallography does remain in university physics departments, but usually either as a characterization ‘service’ (similar to a magnetization or specific heat measurement) or through research groups that are closely linked—and substantial users of—central facilities. In each case, these researchers probably do not prioritize the ‘crystallography’ label since for the former it is one of many techniques being used in their research and for the latter it helps to maintain their distinctive character amongst their central facility-based crystallographic colleagues.

5. Concluding Remarks

The rapid developments of crystallography over the past hundred years have been substantially supported by the work of physicists while at the same time modern physics—especially condensed matter physics—is indebted to crystallography. This is clearly a symbiotic relationship, albeit one that is often unspoken and under-acknowledged. There is a perception that physicists should not brand themselves ‘crystallographers’; indeed even Lawrence Bragg, the founder of x-ray crystallography, was loathe to do so. Pippard summarized physics as ‘physics is what physicists do’ when he wrote about the Cavendish in Cambridge:

‘It is one of the hazards of allowing the greatest freedom to first-class staff that their ideas may not always tally with conventional definitions of physics. It has long been Cavendish policy not to worry overmuch, provided […] the ideas are intellectually worthy. This policy, summed up in the motto ‘Physics is what physicists do’, made the Cavendish thirty years ago the nursery of Molecular Biology […] It is on the cards that some of the most popular research fields will fairly soon be priced out of the market, and a more liberal interpretation of what physics is about will then become commonplace.’ [53]

Tentatively taking this somewhat all-encompassing motto on-board, if a physicist is working on crystallographic problems, then those problems are indeed ‘physics’ irrespective of what their physicist colleagues may claim!

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4 One notable exception to this is my colleague Mike Glazer, who used to even have ‘crystallographer’ in his passport.
