

A Century Plus of X-rays

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As we approach the last quarter of the celebration of the International Year of Crystallography [1] let me relate some of the excitements and the developments that followed the epochal works conducted in 1912 on both sides of the English Channel. I will conclude with a tip of my Stetson to today's champions who are keeping the fire brightly lit well into the twenty-first century.

X-ray techniques have played a pivotal catalytic role in catalysis R&D. The term "catalysis" was introduced by Brezelius in 1835. Later W. Oswald's definition -catalyst as an agent that affects the reaction rate without it being consumed in the process joined the lexicon especially, following his Chemistry Nobel prize of 1909.

The story of x-ray in materials starts at the University of Munich. Where, upon learning from Ewald that the particles inside crystals are regularly spaced by a distance of the order of 1/1000 of the wave length of visible light, Max Laue opined, wave nature of x-rays will be confirmed if upon passing a beam thorough a crystal interference patterns can be produced.

True Laue learnt about lattice size from Ewald, but he was fully aware that at least since the seventeenth century ideas about internal periodicity in crystalline solids have been on record. For instance Laue knew that in a new year's pamphlet (1611) Kepler had remarked on the symmetry of snowflakes. NB: Kepler also had the conviction that the geometric solids polyhedrons are the universal building blocks. 1669 Neils Stensen discovered that crystal faces intersect at characteristic angles. Huygen related birefringence of calcite (1690) to a particular 3-dimensional array of ellipsoidal particles. In 1773 Bergman and 1782 Hauy described crystals to be masonry of tiny identical bricks. To accommodate thermal expansion and elasticity, Seeber (1824) replaced the bricks by spherical molecules placed at positions of equilibrium. Hassel's classification of 32 types of crystals in 1830 was followed by Franz Neumann's (1833) suggestion that crystal symmetries reflect internal physics. Also Millerian indices (1839) preceded the development of 14 translational lattices by Bravais (1850). It is likely that most of this was common academic lore. But the technology to physically test these ideas was not yet available. In 1895 Rontgen discovered x-rays serendipitously while researching electrical discharges in vacuum but its nature and the associated wave length was not immediately apparent.

When on a skiing expedition Laue discussed the idea with Sommerfeld, Wien and others were prompt of raise doubts; but, shortly Walter Friedrich set up an experiment and forthright succeeded in photographing interference patterns by passing x-rays thru a copper sulfate crystal. With this single epochal observation [2,3] the Munich group resolved a whole array of fundamental questions namely, x-rays are short wavelength (high energy) Maxwellian waves, "atoms" exist and inside crystals they form an ordered lattices. However, it will still be many more decades before the dust of atomicity will settle [4].

In Munich, the tremendous significance of the Laue spots must have been clear right away. Because promptly before the publication of the results pertaining to the discovery, Walter Friedrich, Paul Knipping and Max Laue signed a one-page document stating "The undersigned are engaged since 21 April 1912 with experiments about interference

of x-rays passing through crystals". It was deposited by Sommerfeld on 14 May 1912 [5].

As we know today, wave scattering by lattice determine many solid state properties including all-important band structure. But the physics of X-ray scattering in a crystal ala the Munich group was not quite right. The description was under constrained. The Laue-Ewald formula involved three integers each representing the order of interference associated with the three directions of space. This full 3-dimensional scheme conjured up an overabundance of spots. Fewer spots were observed in the Laue pattern and missing spots were misinterpreted as "random" gaps in the incident x-ray spectrum.

Lucky for us, at the same time on the other side of the English Channel a bright young chap, William Lawrence Bragg was taking his National sciences (physics) degree at Cambridge University. His father William Henry Bragg, physics professor at Leeds was aware of the work at Munich and discussed the results with him. Mathematically gifted Lawrence was intrigued by the absence of spots, the changing of shapes from circular to oval as the pattern moved off incidence and also that the pattern turned six degree when a crystal was rotated by just half that angle. Typically, the angular displacements of non-specular interference spots are determined by trigonometric functions and produce highly nonlinear response [6]. Lawrence then barely 22 years old figured that the Laue pattern could not be due to three dimensional lattices but a sub-set associated with interference of x-ray wavelets reflecting off successive atomic planes.

In this specular reflection process there are (only) two relevant lengths, the x-ray wave length θ and the inter-plane distance $d(klm)$ where klm are the Miller indices and the scattering angle (θ). Lawrence Bragg derived the appropriate conditions for constructive interference and obtained a simple eponymous equation that relates the order of the interference (n) and the ratio of the lengths with $\sin(\theta)$;

$$n \lambda / d(klm) = 2 \sin(\theta).$$

Furthermore based on this equation and the missing spots in the Munich Lawrence was able to deduce that the lattice of ZnS is not simple cubic (SC) as presumed by Laue et al but face centered cubic (FCC). Not coincidentally William Barlow another Englishman was the first to introduce SC and FCC and the concept of close packing into crystallography (1833). Shortly thereafter Lawrence left Cambridge to join his father at Leeds. At Leeds their roles can be best described by a phrase from P.W. Anderson (Nobel Physics 1977) "theory on

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tap not on top” [7]. In less than two years the Bragg duo would build new crystallographic equipment including ionization chambers that would produce electrical outputs, a more versatile output signal than photographs. The young Bragg provided the theory (equation) while the senior and experimenter was the progenitor of atomic crystallography and X-ray spectroscopy. To this day, both techniques remain R&D work horses in laboratories all over the globe. Three consecutive physics Nobel prizes in x-ray’s were to follow - Max Laue in 1914, the Braggs shared the same in 1915 (no Nobel in 1916-WW1) and Barkla in 1917. Starting with Rontgen’s first ever prize in 1901 [8-11]. The important role of x-ray in the early twentieth century is marked by it winning four out of the first 16 awards!

Once the principle was mastered it was inevitable that development of neutron and electron diffraction techniques would follow and so would the prizes but this time for all the three areas of the awards Physics, Chemistry and Physiology/ Medicine [12]. A cursory look would reveal the versatility of interference techniques. Linus Pauling (Chemistry 1954) for chemical bonds. The pivotal role of the “X” in Rosalind Franklin’s XRD in determining structure of DNA by Crick, Watson & Wilkins, (Medicine, 1962) prize is well known. Dorothy Hodgkin (Chemistry 1964). Brockhouse & Shull neutron scattering (Physics, 1994). Gerhard Ertl (Chemistry 2007). Shechtmann (Chemistry 2011), imagine the quasicrystals without the 5 fold symmetric diffraction patterns.

A fact often understated is that a direct association exists between “thermo” & x-ray crystallography. This is a pre-natal relationship dating back to the days when the planetary model of the atom, dual nature of matter and quantum mechanics are being formulated or hotly discussed. How random atomic vibrations would affect the propagation of charged particles (electrons) in metals or waves in a crystal were still very much open questions. According to a foot note in the popular solid state physics text book by Charles Kittel [13] one objection to Laue’s idea was that because of thermal fluctuations the instantaneous atomic positions inside a crystal at room temperature deviate from perfect regularity and should smear out any interference pattern.

Fortunately, during the years 1906 and 1909 Max Laue worked on the question of entropy and the thermodynamic significance of the coherence of light as an assistant to Planck, he was well equipped to take up this problem that overlapped much of physics of his time. No wonder the thermodynamic average of scattering cross-section was solved at Munich and is accounted for by the Debye-Waller factor. Remarkably, by the genius of these masters’ this pesky random fluctuation was transformed to be gateway into the inner workings of the material. Today this factor yields a plethora of information [14-16] about the quantum environment of the atoms contributing to the interference pattern.

The most urgent problems of our industrialized society may remain unsolved without the discoveries that took place in one hundred years in the past. Today all over the world many fellow researchers including John Armor, Alex Bell, Bruce Gates, Wayne Goodman, Steven Jacobsen, Caleb A. Kent, Manos Mavrikakis, Gabor Somorjai, [17-22] Sir John M. Thomas [23] and last but not the least my colleague from the chemistry department next door, Richard D Adams [24-26] continue to extend diffractive and spectroscopic tools to new R&D destinations. There will be no surprises if researchers in 2112 will be paying tribute to the advances being made by today’s champions.

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