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Editorial

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The Imperatives in Atomic Structure Analyses: Lessons from Three-Dimensional Diffraction Gratings, Specular Reflection and Quasi- Crystals

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Motivation

A number of challenges in atomic structure in the coming decades lie where the techniques of the past appear to be wanting. The most notable 'up to the minute' exigencies that have taken center stage are the complications of microscopic specimen size and soft order [1,2]. The last problem surfaced with Dan Shechtman's discovery of quasi-crystals [3,4]; systems in which the diffraction pattern defy Bravais classification or the assignment of Miller indices. It exposed a severe inadequacy in Laue-Bragg's famously successful technique in crystallography [5-9]. Furthermore new advances such as high intensity coherent radiation beams, ultrashort exposure and extremely fast detectors, coupled with the desire for atomic resolution in real time, demands a reassessment of the premises of classical crystallography; also it is imperative to find the way to an alternate approach that is indifferent to long-range order and baggage from the associated reciprocal space, leverages the principle of 'reflection-diffraction duality' to embody Bragg's computationally facile top-down approach with Laue's local bottom-up perspective, and (ii) covers a definition of crystal matter that is more inclusive especially the complex regime of partial loosening of order, but not complete disorder.

Overview

The Nobel winning discovery of 'Laue spots' in 1912 is one of the pivotal breakthroughs in history [10]; to this day, over a century later its implications continue to reverberate through the sciences. In 1925 Alver Gullstrand, Chairman of the Royal Swedish Academy of Sciences would declare [11], " *This epoch-making discovery [Laue spots], which not only bore upon the nature of X-radiation and the reality of the space lattice assumed in crystallography, but also placed a new means of research into the hands of Science* …". Paradoxically, although Max Laue anticipated the 'Laue effect', but his new 3-dimensional vector diffraction theory had some serious flaws [12]. As a matter of fact, this theory shockingly misinterpreted the observed patterns. Nevertheless out of Max Laue's fecund but imperfect analogy of three-dimensional diffraction gratings, wave scattering has emerged as a blockbuster success in a wide range of technologies including low energy electron diffraction (LEED), x-ray crystallography (XRD), and x-ray fluorescence (XRF). Techniques helped reveal the geometric structures of the simplest salts as well as the complex double helix spirals of the two strands of polynucleotides in life's genetic code, deoxyribonucleic acid (DNA), netting dozens of Nobel Prizes in Physics, Chemistry and medicine.

A surprise came in the early 1980's with Dan Shechtman's perplexing discovery [3,4] of spot patterns that disturbed the certitude of classical crystallography. This quasi-crystal puzzle would force the International Union the International Union of Crystallography to a redefinition of crystals in 1991 [13]. And in 2011 Shechtman would be honored with the Nobel Prize for chemistry. Here we query where Laue's mathematics slipped and where Bragg's formula really and exactly fits into classical crystallography. Especially re-examine the legacy of Miller indices and the dual space and prompt an improved approach that accommodates current trends and future needs of structure analysis; particularly the concerns of imperfect order, real-space configuration, microscopic specimen size, and extremely short exposures to high intensity beams [1,2,14].

Introduction

In 1912 Max Laue an expert and lecturer of optics in Arnold Sommerfeld's theoretical physics Institute at Ludwig-Maximilians-University (LMU) in Munich, Germany, theorized that if solid crystals comprise of ordered, three-dimensional packing of atoms, then diffraction spots would be produced by passing x-ray waves

through crystals.. In his Nobel Prize lecture [10] Max von Laue described the run up as

> "*the acknowledged masters of our science, … entertained certain doubts about this viewpoint…. A certain amount of diplomacy was necessary before Friedrich and Knipping were finally permitted to carry out the experiment* ".

After Laue's presentation at the Berlin Physical Society on June 8 1912, his former professor Max Planck, a close scientific associate and long-time friend Albert Einstein, the general relativist Karl Schwarzschild (of Black hole fame) and others applauded Laue's prescience.

Albert Einstein

To explain his effect, Max Laue an authority in physical optics proposed that real crystals coherently scatter off x-ray waves, as would a three-dimensional diffraction grating. Notice, that until this time only one and two-dimensional cross gratings were in existence, although the later was of little practical use. But a 3-d grating was totally a new invention. In his Nobel lecture quoted earlier, [10] Laue describes it as

> "*at that point that my intuition for optics suddenly gave me the answer: lattice spectra would have to ensue*".

Guided by an analogy with one and two-dimensional optical gratings 'generalized' to the third dimension, (Figure 1) Laue demanded that at each spot the wave and lattice vectors must satisfy the following set of three 'fundamental equations', as follows

$$\overline{a}_1.(\overline{k}_f-\overline{k}_i)\equiv a_1(k_f cos\phi_f - k_i cos\phi_i)=\overline{a}_1.\Delta\overline{k}=n_x(2\pi) \qquad (1)$$

Likewise

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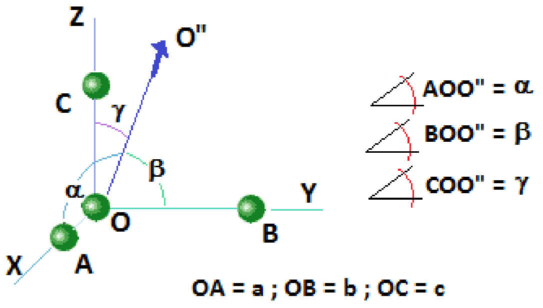

Figure 1: Laue diffraction kernel in an orthorhombic crystal and a ray (OO") in three-dimensional Euclidean space. The four atoms, the Cartesian axes and the ray define three planes, namely XAOO", YBOO" and ZCOO", the angular coordinates of OO" are the three angles (α, β, γ). The lattice vectors are a, b and c respectively.

$$\bar{a}_3.\Delta\bar{k} = n_{z3}(2\pi) \quad (2)$$

and

$$\bar{a}_3.\Delta\bar{k} = n_{z3}(2\pi) \quad (3)$$

The 'dot' in eqs. 1-3, stand for scalar product, angles are measured with respect to the crystal axes and the Laue indices or order numbers nx, ny and nz, are three independent (typically small but not necessarily distinct) integers. In Laue's bottomup description, short-range local order is paramount; the effect of the entire crystal

is modeled by the actions of just the few atoms included in the kernel.

Laue's Achilles heel

Incredibly, it was Max Laue's own 3-d diffraction grating theory that was problematic and consequently failed to interpret Friedrich and Knipping's experimental data [12]. As a matter of fact simultaneously satisfying the dispersive equations along all the three Cartesian axes was overwhelming and Laue's results came out erroneous, including a wrong answer for the crystal density! Incidentally, Laue was aware of some of the problems with his theory, because in his Nobel lecture he stated,

" *... the three specified numbers... I made no secret of the fact that I could not attribute to these values the same degree of reliability...*"

But Max Laue did not realize that he did not properly constrained the system of equations and lacked Euclidean length invariance; so the theory was producing too many solutions [12]. As a matter of fact, it is not generally known that Euclidean geometry and dimensionality of the space-time have a significant influence on what physical phenomena are permissible; vector product and Huygen's principle for wave are two classic peculiarities of 3+1 dimensional space-time [15]. In 3+1 dimensional space-time, generalizing from one-dimensional to two-dimensional gratings is 'trivial' because the angular position of any maximum is completely determined by the grating constant in that particular direction. For example, two cross gratings with same grating constant, b, along y direction but different values of a (along the x-axis), the n_x=2 and ny=1 maximum will be produced, at exactly the same angle β, but at two different values of α, as determined by equation 1. The reader will immediately notice that the angle γ wrt to the z-axis is also different because the angles α, β and γ are not independent, but interlinked by the square of the direction cosine rule, as follows,

$$cos^2\alpha + cos^2\beta + cos^2\gamma \equiv 1 \quad (4)$$

In essence in the space we live in it is impossible to impose three Cartesian components independently of each other as seemingly required by Laue's three fundamental equations 1-3. Consequently, there is a critical theoretical difference between 2-d and 3-d gratings. Allvar Gullstrand, [11] quipped

"*Inasmuch as this is a three-dimensional grating, its effect is in essential respects unlike the effect of the previously known line and cross gratings*".

Reaction to Laue's Effect

William Henry Bragg (WHB) the erstwhile professor of physics at Adelaide, Australia and an acknowledge authority in x-rays, who by this time was a physics professor at Leeds, in UK along with his son William Lawrence Bragg (WLB) took notice of Laue's effect [16-20]. So did Ernest Rutherford's atomic group at Manchester [21,22]. Especially Rutherford's protégé the young and brilliant Henry Gwyn Jeffreys Moseley, Henry Moseley was particularly critical of Laue's theory and in a letter to his mother, he wrote "[Laue] *gave an explanation which was obviously wrong*".

Truth be told, Moseley was notorious for his critical attitude towards fellow researchers as-well-as his own doctoral advisor Earnest Rutherford, 'son of a flax farmer' from New Zealand, a small inconsequential colony in the remotest frontier of the then vast British Empire. Nevertheless Moseley's self-confidence and genius was recognized at Manchester and despite his initial hesitations about jumping on the crystal structure band wagon, Rutherford would let Moseley temporally move to Leeds to learn x-ray spectroscopy, then being invented and developed by WHB. Perhaps not so coincidentally, at the very same time June-August of 1912 Rutherford's visiting 'post-doc' Niles Bohr, would also abruptly change his previous research plan and get busy with a new theory for a stable quantum atom. Mosley made excellent use of his stay at Leeds and upon his return to Rutherford's laboratory back in Manchester atom he would soon invent x-ray fluorescent spectroscopy (XFS) and apply it to discover his name sake Moseley's Law, which relates the frequency (energy) of Barkla's characteristic x-ray emission from the atom with the nuclear charge of the chemical element. As a matter of fact in the process discovering atomic number (Z) and identifying Z with the nuclear charge of the atom. He was a nominee for the Physics Nobel Prize in both 1914 and 1915 and certainly would have been a recipient; because in the same (1925) lecture [11] Alvar Gulstrand also announced that

"*the greatest success by the young scientist Moseley... He further discovered ... what is known as the atomic number, ... has proved to distinguish the elements better than the atomic weight ... Moseley fell at the Dardanelles before he could be awarded the prize* ".

Henry Moseley is recognized as one of the youngest pioneers in nuclear physics. However, it was WLB who proffered a new explanation for Laue's effect that correctly accounted for all the observations and paved the way to atomic crystallography. Incidentally, at that time Bragg was also a student of Joseph John Thomson (Cavendish) and William Jackson Pope (Chemistry) at Cambridge University. Earlier Professor Pope [23] along with the well-known British amateur geologists William Barlow [24] had already developed close packed model structures of various crystals. Barlow was also the first to note the differences between simple cubic and of face centered cubic arrangements of atoms, a point that Laue had completely missed in his analysis, described earlier (Figure 2). William Lawrence Bragg had an empirical and more hands on approach. Noting that when he turned the crystal target by 3o, the whole spot pattern rigidly rotated by 6o, and knowing that generally diffraction patterns follow some complicated trigonometric dependence, Bragg realized that certain planner surfaces in the

crystal must be (partially) reflecting off the x-rays. Apparently, C. T. R. Wilson of cloud chamber fame had a part in this, because in his first paper [16] published in November of 1912 WLB writes,

"… *it was suggested to me by Mr. C.T.R. Wilson that crystals with very distinct cleavage planes, such as mica, might possibly show strong specular reflection of the rays. On trying the experiment it was found that this was so… left no doubt that the laws of reflection were obeyed… bending the mica into an arc, the reflected rays can be brought to a line focus … yet the effect almost certainly not a surface one…* ".

Bragg's focus was on the large-scale geometry, specifically atomic planes but not on local atomic order. He introduced the practice of identifying a spot by the Miller indices (h, k, l); he also proffered the eponymous formula or Bragg's law for the wavelength of x-ray associated with a spot as,

$$n\lambda=2d_B \sin\theta \qquad (5)$$

Where θ is the 'glancing angle' and dB the inter-planer distance and n is the Bragg integer. In equation 5, wave dispersion is effective only along dB a direction perpendicular to the planes. Freed from the direct considerations of 3-dimensional lattice periodicity, Bragg's law also dispenses of Laue's desperate conjectures including the infamous 'missing spot' proposal, invoked to interpret the patterns recorded by Friedrich and Knipping [12]. Unsurprisingly Bragg's formula is computationally frugal. Once again Alver Gulstrand [11] lauded,

"…*It was by a stroke, brilliant in its simplicity, that the Englishman W.L. Bragg succeeded in replacing von Laue's comparatively complicated theory of the effect of the crystal lattice by an extremely manageable formula* …".

In classical crystallography Bragg and Laue's formulations are reconciled by imposing a set of stringent selection rules in this dual space, such that each Bragg reflection spot is associated with a reciprocal lattice node. In his publications Bragg introduced Miller indices for calculating the inter-plane separation distance *d* Bragg. Reciprocal lattice parameters remain central in crystallography. Legacy of the dual space is also apparent in textbooks such as *Solid State Physics*, (p 99-100) by Neil W Ashcroft, N David Mermin [25] where it is explained that "a Laue diffraction peak corresponds to a change in wave vector given by the reciprocal lattice vector ***K*** corresponds to a Bragg reflection from the family of direct lattice planes perpendicular to ***K***. The order, n, of the Bragg reflection is just the length of ***K*** divided by the length of the shortest reciprocal lattice vector parallel to ***K***." Similarly in *Principles of the Theory of Solids*, the author JM Ziman [26] writes, (pp: 52-54) that "To satisfy these geometrical conditions in reciprocal space we construct the *Ewald sphere* with radius OP equal to the incident wave-vector …". It is crucial factor for the convergence of Laue's diffraction with Bragg's reflection is that the scattering system be perfectly crystalline and of sufficiently large extension to posses a reciprocal space.

Quasi-Crystals Challenge Bragg

For almost three-quarters of the last century Bragg's eponymous formula would remain famously unchallenged. Nevertheless, particularly because of its heuristic or semi-empirical rationale, many experts take Bragg's Law as an ansatz to Laue's diffraction theory; for instance the noted author Charles Kittle writes "[Bragg] is simple but is convincing only because it reproduces the results of Laue" [27]. Bragg's law was severely pushed back from the experimental side as well by Dan Shechtman discovery of the illicit five-fold-symmetry in electron diffraction patterns of some rapidly quenched metallic alloys. Upon his initial observation, Dan Shechtman, had reportedly blurted out in his native Hebrew ka,"Eyn chaya zo," (there can be no such creature).

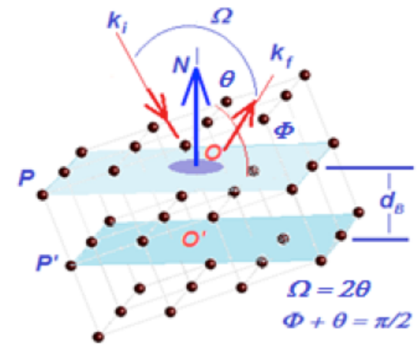

Figure 2: In Bragg's proposal, the highly penetrating X-rays are partially reflected by planes of atoms (two planes P and P' shaded in light blue).

These quasi-crystals are out of bounds of the conventional Bravais lattice classifications and the spots for these puzzling systems cannot be Miller or Bravais indexed. Consequently, neither reciprocal lattice concepts nor Bragg's law are applicable to quasi-crystals. Eventually the accumulated experimental evidence compelled the International Union the International Union of Crystallography to a redefinition of crystals [13]. However, the occurrence of the forbidden symmetry would be too perplexing for some of the leading authorities in crystallography, in particular the two-time Nobel winning chemist Linus Pauling. "*Danny Shechtman is talking nonsense, there are no quasi-crystals, just quasiscientists."*

- Linus Pauling

Lessons from History

The 3-d diffraction grating failed to correctly predict the spots pattern. But Laue's bottom-up theory is based on the tiniest periodic structure, hence the most diffractive part of the whole system– Max Laue's scheme zeroes in on the most relevant length scale. In this sense, Laue was absolutely right- a small organization of atoms and a large crystal with perfect translational order would both produce spots, there can be no question about that. Laue missed important details but had a very fruitful idea. So our first lesson should be as follows-"*It is more important to be fruitful than correct*" - A.N. Whitehead On the other hand Bragg's heuristic law of two-dimensional atomic planes correctly solve structure of perfect crystals. Coincidentally, in 1914 Max von Laue was awarded the Nobel Prize for physics with the official citation, *"for his discovery of the diffraction of X-rays by crystals"*. Apparently Laue was fully cognizant of the success of the interference description and titled his Nobel Lecture [10] as "*Concerning the Detection of X-ray Interferences*"! A system with long-range order may not exist without short-range order, although localized orderly regions may co-exist in a disordered system. As a result Bragg's law fails in quasi-crystal, i.e., systems with short-range order that lack longrange organization.

This brings us to our second lesson, the principle of 'reflection-diffraction duality', that is regardless of the mechanism that bring the wavelets or contribute to the deviation from the rectilinear wave propagation, maxima are obtained only when (where) waves with the correct phase conditions constructively superpose. Hence, diffraction explains spots from quasi-crystals whereas specular reflection is the description for perfect crystals. As a matter of fact, without explicitly invoking reflection-diffraction duality this idea of is often implied; for instance the section on ‘crystal diffraction’ a celebrated textbook [28] describes the relevant physics of wave scattering process as reflection, without ever using the word ‘diffraction’, not even once in the entire text!

Summary

Upon interaction with atoms in a specimen, waves of appropriate phase difference give rise to maxima; the geometric pattern of the maxima provides a faithful map of the spatio-temporal distribution of the atoms. The famous Bragg’s law of classical crystallography is extremely facile and productive but requires perfect crystal specimens. Furthermore lacking a firm theoretical foundation has been a weakness of Bragg’s law. Structure analysis without Bragg’s law is possible in principle but correctly taking into account the diffraction of a large number of atoms requires large computing power. Incorporation of reflection-diffraction duality may permit one to treat coherent wave scattering more economically even in the Laue limit. One strategy is to start with Laue’s three diffraction equations and without the use of the reciprocal lattice mathematically derive the geometrically correct solution. Such a solution will be (i) based on a solid theoretical foundation, (ii) applicable to systems with both short and long range orders, plus (iii) provide benchmarks for comparisons with experimental data. Additionally a fresh understanding is likely to benefit current and future trends toward high intensity radiation, short exposure, decreased order and specimen size plus emphasis on real space visualization.

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