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X-RAY DIFFRACTION

The centennial of X-ray diffraction (1912–2012)

Foreword

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The idea that flashed into Laue's mind in April 1912 is the very reason for the conference held at the Accademia Nazionale dei Lincei (8–9 May 2012) dedicated to the celebration of the *Centennial of X-ray diffraction*. The experiment performed in 1912 was the starting point for a giant leap for science, because it proved, at the same time, that the X-rays were electromagnetic waves and that a crystal had a triperiodic structure at the atomic scale. This opened the way to exploring the atomic and bonding properties of matter, and eventually to understanding the molecular basis of life. Since then, at least two dozen Nobel prizes were awarded in different branches of science, which can be related in some way to crystallography.

The conference was organized jointly by the Accademia dei Lincei and the Accademia delle Scienze di Torino. It was also supported by the Associazione Italiana di Cristallografia (AIC), European Molecular Biology Organization (EMBO), and the University Roma Tre, and was under the patronage of the European Crystallographic Association (ECA). Among others, the conference has had the merit of joining together scientists from different fields—albeit most of them were crystallographers. Hyper-specialization is an unfortunate situation modern science often experiences, but it can still be overcome by mutual information.

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The lectures were given by 16 internationally renowned speakers, among which two Nobel laureates (R. Huber, Germany and J.E. Walker, UK) and one of the recipients of the 2011 Ewald prize (C. Giacovazzo, Italy). Speakers represented many of the different branches of science that were revolutionized by the possibility of mastering the structure of crystalline matter at atomic resolution, and to understand in details the relationships between structure, bonding and reactivity. Their talks covered most aspects of the topic, from the theoretical to the experimental ones, from historical issues to cutting edge research involving mineralogy, material sciences, chemistry, physics, drug design and biochemistry. They were submitted and peer refereed promptly, and published online http://www.springer.com/environment/journal/12210 as soon as they became ready. Unfortunately, three of the speakers could not submit their papers in time. The names of the reviewers—unknown to the authors—will be included, in alphabetical order, in the List of Reviewers this journal publishes periodically to express gratitude for their generous contribution.

The two-day meeting was attended by up to 150 scientists and graduate students coming from all over Italy and from the various branches of science of relevance. They enjoyed the very interesting talks and contributed to lively discussions both during the session time and during the coffee and lunch breaks. Visits to the unique frescoes and the recently renovated Renaissance gardens of Villa Farnesina, opposite to Palazzo Corsini, the Accademia dei Lincei headquarters, as well as a delicious conference dinner in a typical Trastevere restaurant also contributed to strengthen new relationships and exchange ideas on the present and future use of X-ray diffraction and on the frontiers of data interpretation.

The organizing committee (M. Brunori, G. Ferraris, A. Mottana (chair), R. Oberti, R. Righini, P. Rossi, G. Setti, and A. Zecchina) worked hard to make available to the international and Italian community a great opportunity to reflect on the prestigious past of X-ray diffraction, on the most recent achievements, and on the still unforeseeable future of many scientific disciplines in a time when Computer Science is offering incredible new tools for the structure-based approach to reactions, processes, and functional properties of almost any kind of compound in any possible environment. Indeed, the meeting was an excellent introduction to the Italian initiatives to be held during the upcoming International Year of Crystallography (2014).

We, the Supplement Co-editors, take this opportunity to express our appreciation to the speakers, the chairpersons, and all the participants for their contributions to this initiative. In addition, we would like to sincerely thank Francesco P. Sassi, the Editor-in-Chief of *Rendiconti Lincei—Scienze Fisiche e Naturali*, for his firm guidance along the troublesome paths leading to fulfilling such a complex work.

To provide an historical background to the diffraction experiment performed by X-rays under Laue's guidance in 1912 (Friedrich et al. 1912), a short account of the efforts of many scientists to understand the diffraction of the visible part of the electromagnetic spectrum is reported in this Foreword.

Light diffraction was, possibly, noticed by Leonardo da Vinci (ca. 1500), but the evidence of it is controversial.[1] By contrast, there is positive evidence that light diffraction was observed, described on the basis of experiments, and first named and discussed extensively by Francesco Maria Grimaldi, a Jesuit priest from Bologna (2 April 1618–28 December 1653) who was active during the early phase of the "scientific revolution".

Grimaldi (1655) studies of light are to be found in his posthumous book, usually referred to as "De lumine", and in the form of "Propositio" i.e., in the form—traditional at that time among scientists—of a plain statement, followed by its discussion and demonstration. The proposition mentions diffraction as a fourth form of light propagation, in addition to the already well-known three forms: direct (i.e., straight propagation), refraction, and reflection. Then, the entire chapter 1 of Grimaldi's book deals almost entirely with this new form, probably because reflection and refraction had recently undergone mathematical descriptions (Snell' law 1621; Descartes' law 1637).[2] Notably, Grimaldi states in his lengthy attempt of explanation that diffraction occurs because light propagates "undulatim" i.e., as waves. Thus, he is also responsible of introducing a concept that will be harshly debated among physicists for more than three centuries to come.

How did Grimaldi arrive at this experimental observation? He had noticed certain shadows that were not on the straight path of the light beam coming from a thin pinhole, and hence, he concluded that the light would undergo a path deviation that differed from the known one due to refraction,[3] and that the shadows depended upon interference of light waves. Grimaldi had made such an observation using a hand-made but well-constrained geometrical set up, as described. The first experimental section of his book indeed confirms that he was a very good observer and scientist. However, Grimaldi added a second, final section with the attempt to interpret his observations according to the Aristotelian tradition. It is really difficult to judge whether this second section was the personal idea of Grimaldi as a scientist, or if was suggested to him by some Jesuit authority as a precaution against the catholic inquisition. Indeed, this was the cautious mood prevailing among Italian scientists after Galileo's abjuration (22 June 1633); as a consequence, this led to a rapid decline of Italian innovative science. Unfortunately, Grimaldi died (at 45 years of age) while the process of obtaining the *imprimatur* was still going on. Regrettably, inconsistencies in his work hindered the dissemination of his discovery; he died before clarifying his ideas by corresponding with other scientists and cultured men, irrespectively of their religious faith.

Grimaldi's work was mentioned in the first edition (1704) of Isaac Newton's *Optikcs*, based on lectures written down between 1674 and 1679. Later on, however, Newton came to other conclusions, and formulated his own corpuscular theory on the nature of light in contrast to Grimaldi's wave interpretation. Therefore, the word "diffraction" disappeared in the second edition of *Opticks* (1718) and in all the following ones, being substituted by "inflection" i.e., a bending of the corpuscles the light is made of. To add up to Grimaldi's accelerated fading out of the scientific scene, only 4 years later (1669) Erasmus Bartholinus detected and described double refraction. Such an extraordinary behavior of light in crystalline materials

[1] The claim is to be found in Libri (Libri 1840, vol III, p 55): "[*Léonard a fait la*]… *observation de la diffraction (8)*". However, this note 8 here only refers back to a Note XVIII at the end of the volume (p 234), which contains nothing directly related to such a phenomenon.

[2] The refraction law had been first described by the Persian scientist Abu Sa'd al-'Ala' ibn Sahl, who wrote in Arabic a treatise *On Burning Mirrors and Lenses* (984 A.D.). He used it to derive lens shapes that focus light with no geometric aberrations. Both Snell and Descartes proposed mathematical formulations of it, the former in an unpublished manuscript, and the latter as a chapter in his seminal book *Discour sur la méthode* (Leiden 1637).

[3] "*Lumen aliquando per sui communicationem reddit obscuriorem superficiem corporis aliunde, ac prius illustratam*". Nowhere Grimaldi attempts at using reflection to explain the unusual shadows he had observed.

shifted the attention of all scientists of the time (among them Robert Hooke, Christiaan Huygens, and Isaac Newton too) and focussed their efforts on its interpretation. Meanwhile, Newton's authority (and his notorious bad character) could impose the corpuscular theory on the nature of light, which entailed straight motion and no diffraction at all. Even Huygens, who believed in the wave theory, fell into shadows, at least till the end of the 18th century.

Light diffraction was independently rediscovered by two of the greatest physicists of the early 19th century: Thomas Young and Augustin-Jean Fresnel.

Young was totally isolated as a scientist working on this subject, and yet he could publish the account of a critical experiment performed successfully on 24 November 1803 at the Royal Society (Young 1804). Such an experiment established forever the wavy propagation of light, but also made him very unpopular among academics. With this single experiment, Young determined the difference in wavelength between red and blue light, and gave a clear physical demonstration of light diffraction. He made a thin ray of sunlight pass through a narrow slit[4] and then forced the passed through light to pass again through two similar narrow slits placed next of each other, till to finally impinge onto a screen. The two light rays did not follow a straight path but spread apart and overlapped, and in the overlapping area bright bands alternated with dark bands.

Fresnel worked over a time when there was in France a whole group of inspired scientists who dedicated themselves to optics in a spirit of occasionally harsh but always healthy competition (e.g., Etienne Louis Malus, Jean-Baptiste Biot, and Dominique-François Arago). Fresnel started studying light diffraction in 1815 and almost immediately was advised by Arago of Young's works, as well as Grimaldi's and Newton's, in a personal letter.[5] Fresnel took the advice gratefully, but he answered pointing out that he could not take advantage of Young's works but in a very minor amount, because he did not know English.[6] He went on independently, and reached results that Thomas Young could never have reached because of his different approach. Indeed, Young was experimentally minded, whereas Fresnel had a mathematical mind and developed not only new mathematical methods (e.g., Fresnel's integrals), but he was sure that he could predict phenomena even in the absence of the relevant experiment.

When Fresnel competed for a prize awarded by the Académie des Sciences (Paris) on 20 July 1818, he submitted a theoretical essay about diffraction, which was based entirely on mathematically treating light as being a wave motion. He had already met opposition because of his assumption that light and sound behaved in the same way.[7] But Fresnel brushed this opposition aside and went on with verifying his theory by simple experiments. Mathematics had made Fresnel conclude that light deviates from the straight path and produces a sequence of shadows and lights, fading out without a sharp end.[8]

Young and Fresnel had worked independently, and yet they were reciprocally informed of their results. There is a famous report written by Arago of his visit to Young's home in 1816, where he exposed Fresnel's preliminary results and the ensuing theory. After a while, Young's wife, who was silently attending the get-together, stood up and again silently showed to Arago a graph that matched exactly Fresnel's one, and had been hand-written by her husband in a course of lectures he had given as early as in 1807.[9] This settled the question of priority, at least between them.

For the entire century that followed and up to 1912, the wave nature of light and its diffraction became progressively better understood thanks to the theoretical advances by James Clerk Maxwell (1865), Gustav Kirchhoff (1882), Henri Poincaré (1892) and, eventually, to everybody's satisfaction, by Arnold Sommerfeld (1896). However, the main aim of those giants of physics was to unveil the nature and behavior of light. Clarifying diffraction was a minor affair, a consequence inherent the main theory rather than the purpose of their studies. Sommerfeld's definition, in all his candour, is clear on this point: any deviation of light rays from rectilinear in the presence of a screen is impossible; it must be the result of diffraction as it cannot be interpreted as either reflection or refraction. Max Planck,

[4] Actually, it was "*a slip of cards, about one thirtieth of an inch in breadth*" held edgewise (Young 1804, p 2).

[5] "*Je ne connais pas d'ouvrage qui renferme la totalité des expériences… sur la lumière. M. Fresnel ne pourra se mettre au courant de cette partie de l'optique qu'en lisant l'ouvrage de Grimaldi, celui de Newton,… et les mémoires d'Young*" (Fresnel et al. 1866, p. 6). Arago was well aware that Young in Britain had become a scientific outcast due to his experiment that demonstrated that Newton was wrong. His letter, then, was a friendly but covered advice to Fresnel, who wanted to enter into a field marked by conflict.

[6] "*Quant à l'ouvrage d'Young,…, j'avais fort envie de le lire, mais ne sachant pas l'anglais, je ne pouvais l'entendre qu'avec le secours de mon frère et, après l'avoir quitté, le livre redevenait inintelligible pour moi*" (p 7 in Fresnel et al. *cit*.).

[7] "*La plus forte objection qu'on ait faite à cette théorie est celle qui est fondée sur la comparaison de la lumière et du son*" (p 12 in Fresnel et al. *cit*.).

[8] "*Cette objection, la seule à laquelle il me paraisse difficile de répondre complètement, m'a conduit à m'occuper des ombres portées. J'ai observé que les ombres n'étaient jamais terminées nettement comme elles devraient l'être si la lumière ne se propageait que dans le sens de sa direction primitive. On voit qu'elle se répand dans l'ombre, et il est difficile d'assigner le point où elle s'arrête, les limites de l'angle d'inflexion. J'ai vu de la lumière jusque dans le milieu de l'ombre d'une règle de deux centimètres de largeur*" (p 12 *in* Fresnel et al. *cit*.).

[9] Now in print as Fig. 267 on Plate XX at p 776 in Young (1845).

with his quantum theory (1900), and Albert Einstein, with his photon and his photoelectric effect (1905), were also interested in light first (or only); they made no attempt at exploring any phenomena that would arise when using the entire electromagnetic spectrum.

When in 1912 Max Laue conceived his idea of investigating the behavior of matter by impinging directly an X-ray beam, he saw in the first picture taken by Walter Friedrich and Paul Knipping a few grey round spots all around the large black shadow marking the straight path to the crystal acting as screen and target. He probably recalled the definition of diffraction given by his mentor Sommerfeld[10], but he did not use the word diffraction in the title of his seminal paper and preferred to mention generically the interference among X-rays instead. Anyway, he dismissed a priori the simple interpretation William Lawrence Bragg was going to give a few months later ("specular reflexion" by atomic planes: 1912),[11] and went on to concoct a cumbersome formalism which nevertheless makes more physical sense, and is largely made use of in the "electronic era" i.e., now, when computers overcome easily the mathematical difficulties inherent in the original approach.

The state-of-the art in solid state science after Laue's discovery shows that diffraction has become a very popular and very productive method. Nobel Prizes were awarded for several years to people working preferably with X-ray diffraction, irrespectively in physics and chemistry. The number of crystal structures solved so far ranges well over half a million (ca. 150,000 inorganic, over 400,000 organic and complex, and 50,000 proteins and nucleic acids, mostly solved by single crystal X-ray diffraction). This number would include not only natural materials such as the minerals and various biological compounds, but also an exponentially growing number of synthetic compounds.

While the first half of the 20th century saw the revolution of physics and the amazing development of chemistry, the second half was marked by the birth of the new biology, starting with the discovery of the double helix, the secret of life. The extraordinary success of molecular and structural biology is too widely known to require an outline in this foreword. The history of the events leading to the publication of the three-dimensional model of DNA by James Dewey Watson and Francis Crick has been the topic of many books and articles, starting with "The double helix" (1968), a very controversial description of the facts behind the discovery written by Watson himself. This breakthrough, considered the very beginning of a new era and the foundation of modern medicine and of biotechnology, was made possible by the talent of a small group of minds working together in Cambridge in the laboratory founded by Max Ferdinand Perutz following the footsteps of John Desmond Bernal and Lawrence Bragg. As a matter of fact, building the model of the double helix was possible thanks to the X-ray diffraction images of DNA collected by Rosalind Franklin while working in London (Maddox 2002). The cover page of this volume depicts Franklin's famous "Photo 51" universally recognized to have been crucial to crack the structure of DNA. Over the same time span, the pioneering titanic work of Max Perutz and John Cowdery Kendrew led to unveil the three-dimensional structure of hemoglobin and myoglobin, the first proteins to be solved by X-ray diffraction (an achievement made possible by the introduction of the isomorphous replacement method). Their work opened a window on the immense universe of proteomics, so fashionable nowadays.

These fundamental discoveries at the origin of structural molecular biology led, over the past 50 years, to a large number of unexpected findings recognized with the Nobel Prize. Since the birth of the new biology, the introduction of substantial methodological advances (such as genetic engineering, computational methods, synchrotron sources, etc.) made this revolution a reality (e.g., Perutz 1987). Over-and-above these technological innovations, however, the fundamental ingredients of success in structural biology may be traced back to stimulating interactions between sharp committed brains, to long-term stable funding by public sources, and to inspiration by tenured research leaders supporting the attack on fundamental and difficult problems.

Yet, it all started in 1912 with Laue's X-ray diffraction experiment that the Lincei decided to celebrate with this meeting.

[10] "*Paralleles Licht ist bei Verhandensein eines Schirmes unmöglich*" (Sommerfeld 1896, p 366).

[11] This short paper looks very much as Grimaldi's *Propositio*: it is the enunciation of the law, which was explained and demonstrated during the following year (Bragg and Bragg 1913).

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