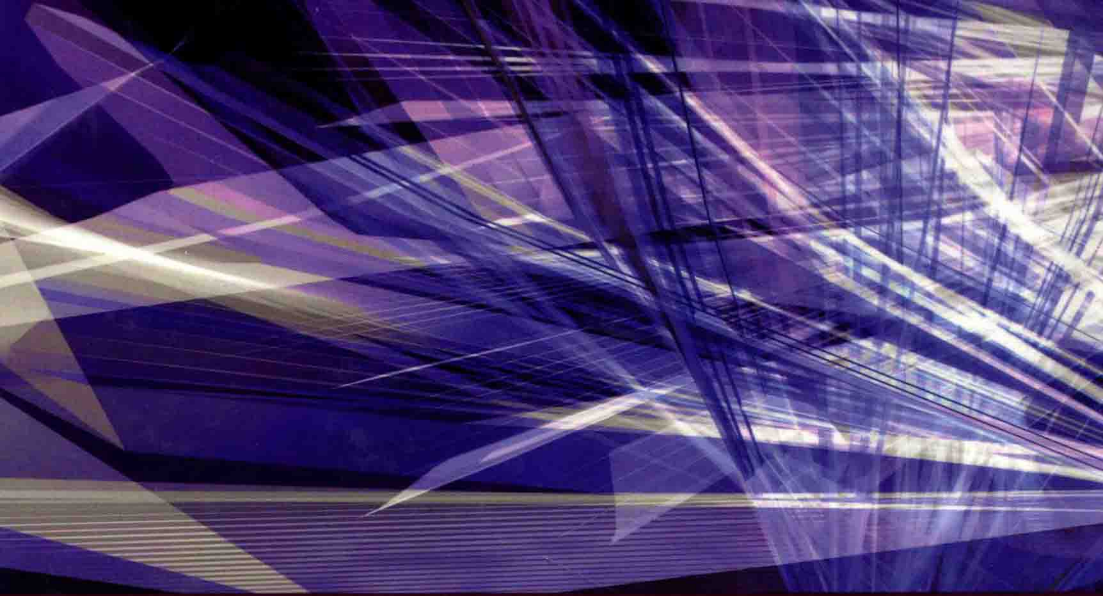

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X-ray Diffraction by Polycrystalline Materials

Preface

In 1912, when M. Laue suggested to W. Friedrich and P. Knipping the irradiation of a crystal with an X-ray beam in order to see if the interaction between this beam and the internal atomic arrangement of the crystal could lead to interferences, it was mainly meant to prove the undulatory character of this X-ray discovered by W.C. Röntgen 17 years earlier. The experiment was a success, and in 1914 M. Laue received the Nobel Prize for Physics for the discovery of X-ray diffraction by crystals. In 1916, this phenomenon was used for the first time to study the structure of polycrystalline samples. Throughout the 20th century, X-ray diffraction was, on the one hand, studied as a physical phenomenon and explained in its kinematic approximation or in the more general context of the dynamic theory, and on the other, implemented to study material that is mainly solid.

Obviously, the theoretical studies were initially conducted on single crystal diffraction, but the needs for investigation methods from physicists, chemists, material scientists and more recently from biologists have led to the development of numerous works on X-ray diffraction with polycrystalline samples. Most of the actual crystallized solid objects that we encounter every day are in fact polycrystalline; each crystal is the size of a few microns or even just a few nanometers. Polycrystalline diffraction sampling, which we will address here, is actually one of the most widely used techniques to characterize the state of the "hard" condensed matter, inorganic material, or "soft", organic material, and sometimes biological material. Polycrystalline samples can take different forms. They can be single-phased or made up of the assembling of crystals of different crystalline phases. The orientation of these crystals can be random or highly textured, and can even be unique, in the case for example of epitactic layers. The crystals can be almost perfect or on the contrary can contain a large number of defects. X-ray diffraction on polycrystalline samples enables us to comprehend and even to quantify these characteristics. However, the methods of measure must be adapted. The quality of the quantitative result obtained greatly depends on the care taken over this measure and in particular on the right choice of equipment and of the data processing methods used.

This book is designed for graduate students, as well as engineers or active researchers studying or working in a sector related to material sciences and who are concerned with mastering the implementation of X-ray diffraction for the study of polycrystalline materials.

The introduction recounts the history of the emphasis on X-ray diffraction by crystals since the discovery of X-rays. The book is then divided into two parts. The first part focuses on the description of the basic theoretical concepts, the instrumentation and the presentation of traditional methods for data processing and the interpretation of the results. The second part is devoted to a more specific domain which is the quantitative study of the microstructure by X-ray diffraction.

The first part of the book is divided into four chapters. Chapter 1 focuses on the description of the theoretical aspects of X-ray diffraction mainly presented as a phenomenon of interference of scattered waves. The intensity diffracted by a crystal is measured in the approximations of the kinematic theory. The result obtained is then extended to polycrystalline samples. Chapter 2 is entirely dedicated to the instrumental considerations. Several types of diffractometers are presently available; they generally come from the imagined concepts from the first half of the 20th century and are explained in different ways based on the development of the sources, the detectors and the different optical elements such as for example the monochromators. This chapter is particularly detailed; it takes the latest studies into account, such as the current development of large dimension plan detectors. Modern operation of the diffraction signal is done by a large use of calculation methods relying on the computer development. In Chapter 3, we will present the different methods of extracting from the signal the characteristic strength of the diffraction peaks including the position of these peaks, their integrated intensity and the shape or the width of the distribution of intensity. The traditional applications of X-ray diffraction over polycrystalline samples are described in Chapter 4. The study of the nature of the phases as well as the determination of the rate of each phase present in the multiphased samples are presented in the first sections of this chapter. The structural analysis is then addressed in a relatively condensed way as this technique is explained in several other international books.

The second part of the book focuses on the quantitative study of the microstructure. Although the studies in this area are very old, this quantitative analysis method of microstructure by X-ray diffraction has continued to develop in an important way during the last 20 years. The methods used depend on the form of the sample. We will distinguish the study of polycrystalline samples as pulverulent or massive for thin layers and in particular the thin epitactic layers. Chapter 5 is dedicated to the theoretical description of the influence of structural flaws over the diffusion and diffraction signal. The actual crystals contain a density of varying punctual, linear, plan or three-dimensional defects. The presence of these defects modifies the diffraction line form in particular and the distribution of the diffused or diffracted intensity in general. The influence of these defects is explained in the kinematic theory. These theoretical considerations are then applied in Chapter 6 to the study of the microstructure of polycrystalline pulverulent or massive samples. The different methods based on the analysis of the integral breadth of the lines or of the Fourier series decomposition of the line profile are described in detail. Finally, Chapter 7 focuses on the study of thin layers. Following the presentation of methods of measuring the diffraction signal in random or textured polycrystalline layers, a large part is dedicated to the study of the microstructure of epitactic layers. These studies are based on bidimensional and sometimes three-dimensional, reciprocal space mapping. This consists of measuring the distribution of the diffracted intensity within the reciprocal lattice node that corresponds to the family of plans studied. The links between this intensity distribution and the microstructure of epitactic layers are presented in detail. The methods for measuring and treating data are then explained

The book contains a large number of figures and results taken from international literature. The most recent developments in the views discussed are presented. More than 400 references will enable the interested reader to find out more about the domains that concern them.

Acknowledgements

X-ray diffraction is a physical phenomenon as well as an experimental method for the characterization of materials. This last point is at the heart of this book and requires illustration with concrete examples from real experiments. The illustrations found throughout this book are taken from international literature and are named accordingly. Many of these examples are actually the result of studies conducted in the last 15 years in Limoges in the Laboratoire de Science des Procédés Céramiques et de Traitements de Surface. My profound thanks to the students, sometimes becoming colleagues, who by the achievement of their studies have helped make this book a reality. I would like to particularly acknowledge O. Masson and A. Boulle in Limoges for their strong contribution to the development X-ray diffraction on polycrystalline samples and epitactic layers respectively.

One of the goals of this book is to continually emphasize the link between the measuring device, the way in which it is used and the interpretation of the measures achieved. I am deeply convinced that in experimental science only a profound knowledge of the equipment used and the underlying theories of the methods implemented can result in an accurate interpretation of the experimental results obtained. We must then consider the equipment that has helped us conduct the experimental study as the centerpiece. Because of this conviction, I have put a lot of emphasis on the part of this book that describes the measuring instruments. I learned this approach from the experience of A. Dauger who has directed my thesis as well as during the years following my research studies. He is the one who introduced in Limoges the development of X-ray diffusion and diffraction instruments, and I thank him for his continued encouragement in this methodology.

Ever since the first edition written in French and published in 2002, several colleagues have commented on the book. These critiques led me to completely redo the structure of the book, in particular separating the conventional techniques from the more advanced techniques linked to the study of microstructure. I would once more like to thank A. Boulle, now a researcher at the CNRS and also M. Anne, director of the Laboratoire de Cristallographie in Grenoble, whose comments and encouragement have been very helpful.

An Historical Introduction: The Discovery of X-rays and the First Studies in X-ray Diffraction

X-rays and "cathode rays": a very close pair

On November 8th, 1895, Röntgen discovered by accident a new kind of radiation. While he was using a Crookes tube, he noticed a glow on a plate, covered with barium platinocyanide, and rather far away from the tube. Röntgen, who was working at the time on the cathode rays produced by Crookes tubes, immediately understood that the glow he was observing could not be caused by this radiation. Realizing the importance of his discovery, and before making it known to the scientific community, he tried for seven weeks to determine the nature of this new kind of radiation, which he named himself *X-Strahlen*. On December 28th, 1895, Röntgen presented his observations before the Würzburg Royal Academy of Physics and Medicine [RON 95]. His discovery was illustrated by the photographic observation of the bones in his wife's hand (see Figure 1). Röntgen inferred from his experiments that the Crookes tube produced beams that propagated in straight lines and could pass through solid matter [RON 95, RON 96a, RON 96b, RON 96c]. Very quickly, these "Röntgen rays" were used in the medical world to produce radiographies [SWI 96].

Immediately after this discovery, a large number of studies were launched to find out the nature of this radiation. Röntgen tried to find analogies between this kind of radiation and visible light, which lead him to conduct unsuccessful experiments that consisted of reflecting X-rays on quartz, or lime. He believed he was observing this reflection on platinum, lead and zinc [RON 95, RON 96b]. He noticed that X-rays, unlike electronic radiation, are not affected by magnetic fields. Röntgen even tried, to no avail, to produce interference effects in X-rays by making the X-ray beam pass through holes [RON 95]. The analogy between X-rays and visible light prompted researchers to study how X-rays behave with regard to the well-known laws of optics. Thus, Thomson [THO 96], Imbert and Bertin-Sans [IMB 96], as well as Battelli and Garbasso [BAT 96], showed in 1896 that specular reflection was not possible with X-rays, hence confirming the studies of Röntgen. They also found, in agreement with the works of Sagnac [SAG 97a], that the deviation of X-rays by refraction is either non-existent or extremely small.

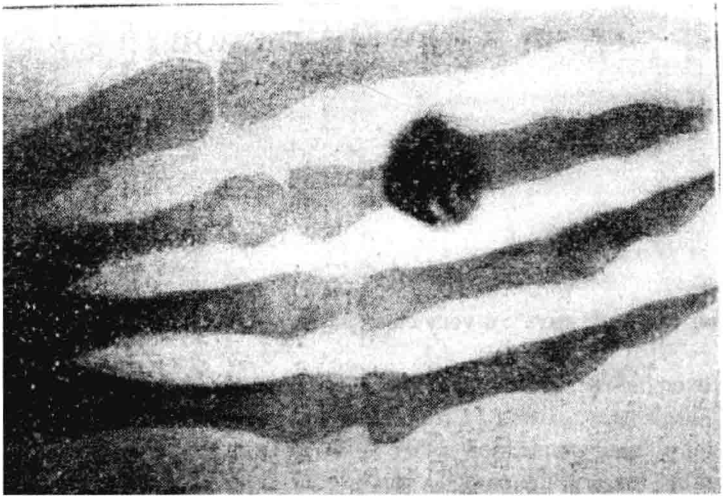

Figure 1. *The first radiographic observation*

In November 1896, Stokes gave a short presentation before the Cambridge Philosophical Society, explaining some of the fundamental properties of X-rays [STO 96]. He claimed that X-rays, like γ-rays, are polarizable. This comment, made in November, did not take into account several studies, even though they had been published in February of the same year by Thompson [THO 96a], who established the absence of polarization in X-rays by having them pass through oriented crystal plates. The polarizable nature of X-rays was conclusively demonstrated in 1905 by Barkla [BAR 05, BAR 06a]. Based on the absence of refraction for X-rays, Stokes described this radiation as vibrations propagating through solid material between the molecules of this material. Finally, by analyzing the absence of interference effects for this radiation, he concluded that either the wavelength of this propagation was too small or the phenomenon was not periodical. The author, who mistakenly believed that the latter hypothesis was the right one, assumed that each "charged molecule[1]" that hit the anode emitted a radiation, the pulsation of which was independent of the pulsations of the radiations emitted by the other molecules.

Having demonstrated that X-rays are a secondary radiation caused by what was referred to at the time as "cathode rays", Röntgen showed that the study of the nature of X-rays had close ties with the determination of the nature of electronic radiation. After the discovery by Crookes of the existence of a radiation emitted by the cathode and attracted by the anode, the question of the nature of these cathode rays was the subject of intense activity. When X-rays were discovered, the two theories clashed. Some considered that this cathode rays was caused by a process of vibration taking place in the rarefied gas inside the tube (the "ether") [LEN 94, LEN 95], while others thought that this current was the result of the propagation of charged particles emitted by the cathode [PER 95, THO 97a].

In 1895, Perrin proved experimentally that the cathode rays carried an electric charge and that this charge was negative [PER 95]. This view was the one supported by Thomson [THO 97a, THO 97b], who published an article in 1897, considered to be the major step in the discovery of the electron [THO 97b]. He noticed that these cathode rays could be diverted by an electrical field. This observation led him to demonstrate experimentally that this radiation was caused by the motion of charged particles, for which he estimated the charge to mass ratio. He found that this ratio e/m is independent of the nature of the gas inside the tube and established the existence of "charged particles", which are the basic building blocks of atoms [THO 97b].

This is how Thomson became interested in X-rays while studying electronic radiation. In January 1896, he presented an analysis that could be described as the "theoretical discovery of X-rays". He used the Maxwell equations and included the contribution from a convection current caused by the motion of charged particles. He demonstrated analytically that these particles suddenly slowing down led to an electromagnetic wave that propagated through the medium with an extremely low wavelength [THO 96b]. The author himself noted that the properties of the radiation discovered by Röntgen were not sufficiently well known to be able to say that the electromagnetic waves he had found evidence of were, in fact, Röntgen radiation. Two years later [THO 98a], Thomson was more assertive and concluded that the radiation related to the sudden slowing down of charged particles – later referred to as braking radiation – was a kind of X-ray radiation.

By analogy with the characteristics of electron radiation, many authors imagined that X-rays also corresponded to the propagation of particles. This debate over the particle or wave-like nature of electromagnetic radiation only comes to a close with

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[1] The concept of electron was only definitively accepted the following year.

the advent of quantum physics. This is why, after the studies of Thomson, several authors compared the respective properties of X-rays and electrons [LEN 97, RIT 98, WAL 98]. Lenard [LEN 97] showed, on the one hand, that irradiating photographic plates with X-rays caused a much weaker effect than what was observed when the same plates were irradiated with an electron beam. On the other hand, he showed that the two kinds of radiation had significantly different electric properties. Ritter von Geitler [RIT 98] irradiated flat metal screens with X-rays in order to find evidence of a possible charge carried by these particles. He did not observe an electrical signal, but nonetheless he did not conclude that the particles were not charged. In the same issue of the *Annalen der Physik und Chemie*, Walter [WAL 98] was more assertive and considered that the particles associated with X-rays have no electric charge. Furthermore, given the high penetrating ability of X-rays, he refuted a theory, acknowledged at the time, according to which X-rays could consist of the incident electrons that had lost their charge after hitting the anode [VOS 97].

Thus, before the beginning of the 20th century, it was accepted as fact that X-rays were very different from the electronic radiation that created them. Scientists also knew that they consist of particles that are not charged, since they are not diverted in a magnetic field [STR 00]. The theoretical works of Thomson describe the propagation of X-rays as that of a wave with a very small wavelength. Furthermore, these X-rays do not seem to be reflected of refracted under conditions that would generally be used to observe these effects with visible light. While some authors were trying to discover the nature of X-rays, other authors were studying the effects of having X-rays travel through gases.

In 1896, Thomson and Rutherford [RUT 97, THO 96c] showed that irradiating a gas with an X-ray beam created an electrical current inside this gas. They showed that the intensity of this current depends, on the one hand, on the voltage applied to the two terminals of the chamber containing a gas, and on the other hand, on the nature of this gas. Rutherford [RUT 97] also observed that the decrease in the X-ray beam's intensity due to the absorption by the gas follows an exponential law which depends on a coefficient specific to each gas. From these findings, Rutherford measured the linear absorption coefficient of several gases and found a correlation between this coefficient and the intensity of the electrical current, produced by the interaction between this gas and the X-rays. In a commentary on Rutherford's article, Thomson [THO 97c] observed that his colleague's findings were evidence of a strong analogy between X-rays and visible light, and that they were likely to be electromagnetic waves or pulses. He also attributed the decrease in the intensity of the X-ray beam, observed by Rutherford, to the production of ions from the gas molecules, with each ionization leading to a small decrease in the beam's intensity.

Based on these first accomplishments, the ionization of gases was used to study the nature of the particles created from the interaction between the X-rays and the gas. By using a cloud chamber designed in 1897 by Wilson [WIL 97], Thomson [THO 98b] used the ionization of gases by X-rays to measure the electric charge of the electrons[2] created by the X-rays traveling through the gas. By measuring the electrical current produced by the ionization of various polyatomic gases, the same author showed that the electrons correspond to a modification of the atoms themselves, rather than to the simple dissociation of gas molecules [THO 98c]. This result was confirmed by Rutherford and McClung [RUT 00], who measured, in 1900, the energy required for the ionization of certain gases. This is how they showed that an electron accounts for a very small part of the mass in an atom.

We mentioned above that, at the dawn of the 20th century, the nature of X-rays was already well known. Evidence of gas ionization by X-rays quickly led to the creation of devices designed to quantitatively measure the intensity of X-ray beams. This enabled researchers at the beginning of the last century to study in detail the interaction between X-rays and solid matter, leading, naturally, to the observation and quantitative analysis of scattering, and then diffraction, of X-rays.

Scattering, fluorescence and the early days of X-ray diffraction

Scattering and fluorescence

In 1897, Sagnac [SAG 97a, SAG 97b] observed that, by irradiating a metal mirror with an X-ray beam, the mirror would produce a radiation of the same nature as the incident beam, but much less intense. This radiation propagates in every direction and therefore cannot involve specular reflection. Sagnac noted that the intensity of this scattered radiation depends on the nature of the material irradiated with the primary X-ray beam [SAG 97b, SAG 99]. These experiments were confirmed by Townsend [TOW 99], who quantitatively measured the intensity of the scattered beams by using an ionization detector. Townsend observed that if the scattered beams, before reaching the detector, pass through a sheet of aluminum, then the residual intensity significantly depends on the nature of the scattering material. Unfortunately, he did not specify the chemical nature of the anticathode he was using to produce the primary X-rays, thus making it difficult to make the connection between this observation and a selective absorption effect.

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[2] In the paper in question, Thomson and other authors use the word "ion", but are actually writing about electrons created by the X-ray-induced ionization. In this case, the word ion is merely the present participle of the Greek verb *ienai*. Therefore, *ion* means going, and refers to particles in motion.

As we have mentioned already, Thomson showed that when a charged particle slows down, it causes the emission of electromagnetic radiation [THO 96b, THO 98a]. Based on these considerations, the same author found a simple explanation to the scattering effect observed by Sagnac. By assuming that the atoms contain charged particles, irradiating these atoms with an electromagnetic wave (the X-rays) would disturb the trajectory of these particles and modify their speed. This explained the subsequent emission of secondary X-rays [THO 98d]. Starting with this simple demonstration, Thomson calculated the intensity of the beam scattered during the interaction between an electron and an X-ray beam. This calculation led him to the now famous Thomson formula, which gives the scattering power of an electron. Once these preliminary results had been achieved, several authors, between 1900 and 1912, characterized in detail this secondary emission phenomenon, which would later come to be called scattering.

In 1906, Thomson [THO 06a, THO 06b] showed that the intensity of the scattered beam increases with the atomic mass of the scattering elements. He measured the intensity of the scattered beams by using a crude ionization detector, in which the ionized gas is the air located between the surface of the sample, consisting of a flat plate or a powder, and a metal grating placed a few millimeters away from that surface. He managed, nevertheless, to establish a direct link between the atomic mass of over 30 elements of the periodic table and the intensity scattered by these elements [THO 06b]. Also, he noticed that the scattered intensity increases with the atomic number, but this relation is not strictly linear: there are gaps in the intensity (see Figure 2). Thomson noted that the position and the amplitude of these intensity gaps directly depend on the nature (hard or soft) of the X-rays used.

These discontinuities in the emitted intensity were studied from a more general perspective by Barkla and Sadler [BAR 06b, BAR 08a, BAR 08b, BAR 08c, SAD 09]. These two authors presented a combined analysis of secondary emission and absorption of X-rays by solid matter. The characteristics of the scattered radiation were investigated by measuring their intensities after absorption by a sheet of aluminum with a known thickness. Barkla showed by this way that there are sharp discontinuities in the graphs showing the emitted intensity or the absorption coefficient plotted according to the atomic number of the irradiated material, located in the same places [BAR 08c]. The positions of these discontinuities do not depend on the intensity of the primary beam, but only on its "hardness[3]" [BAR 08a]. This author makes a distinction between two effects involving the secondary beams emitted by the irradiated substances: he observes, as Thomson did, the presence of a diffuse signal with characteristics similar to the incident beam, and also a more intense signal with characteristics specific to the nature of the irradiated element. Barkla adds that this emission of X radiation involves the ejection of electrons from

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[3] The words energy and wavelength were not yet used at the time.

the atoms irradiated by the primary beam. This ejection disturbs the atoms and results in the emission of an electromagnetic wave specific to the atom in question [BAR 08b]. The works of Barkla, which were quickly confirmed by the results of other authors [CHA 11, GLA 10, WHI 11], constituted the first evidence of X-ray fluorescence, whose developments in elementary analysis are still known today.

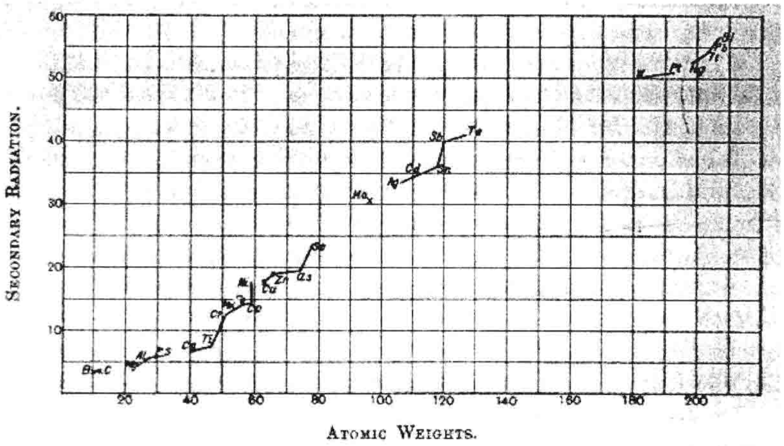

Figure 2. *Evolution of the scattered intensity according to the atomic masses of the scattering atoms (Thomson, 1906 [THO 06b])*

All of these studies led by Thomson, Barkla and Sadler, involving the secondary radiation emitted by solids irradiated with X-ray beams, were consistent with the results of Thomson described above, and tend to show that this secondary emission is the result of an interaction between the electrons of the atoms and the electromagnetic wave, associated by Thomson and Barkla with the X-rays. This wave description was disputed by Bragg [BRA 07, BRA 11], who considered that, if X-rays are "energy bundles" concentrated in extremely small volumes, as Thomson claimed, then they should be diverted when they travel through the atoms. The concept developed by Thomson leads to the assumption that the radiation scattered by the irradiated atoms is isotropic and, in particular, independent of the incident beam's direction of propagation. This is why Bragg focused on experimentally proving that the intensity distribution of secondary X-rays is not isotropic [BRA 07, BRA 09]. Barkla refuted Bragg's arguments in favor of a particle-based description of X-rays, by showing that it would be very difficult otherwise to account for the polarizable nature of X-rays [BRA 08a]. He added that wave theory can account for a certain anisotropy in the distribution of the scattered intensity, since the intensity would be higher in the incident beam's direction of propagation than it would in the perpendicular direction. This argument did not convince Bragg and Glasson, who showed that the intensity of radiation that has traveled through a thin plate of scattering material is greater than that measured on the side of the incident beam [BRA 09].

Crowther presented a series of articles on how to experimentally determine the shape of the intensity distributions for the secondary X-rays emitted by thin plates irradiated with primary X-rays [CRO 10, CRO 11a, CRO 11b, CRO 12a, CRO 12b]. This way, and in agreement with Bragg, he showed that the intensity of the secondary radiation is much greater on the side opposite to the surface irradiated by the incident beam. Crowther notes [CRO 12a], however, that this is not enough to settle on the nature of X-rays with regard to the wave theory or the particle theory. This led him to think that a second phenomenon occurs on top of classical scattering, corresponding, for example, to the emission of X-rays, associated with the emission of electrons inside the materials irradiated by the primary X-ray beam. This interpretation was in perfect agreement with the works of Barkla and Sadler [BAR 08b] who, as we have mentioned before, were the first to observe X-ray fluorescence. Therefore, in the end, the anisotropic shape of the secondary X radiation's intensity distribution was interpreted as the result of a combination of two different types of emission: scattering and fluorescence [BAR 11].

X-ray diffraction by a slit

While some were studying the nature of secondary X-ray emission, other authors, Germans mostly, conducted experiments in order to observe X-ray diffraction by very thin slits. Given the fact that X-rays are similar to visible light, and due to their high penetrating ability, which means that their wavelengths must be very small, these authors surmised that they would be able to observe Fresnel diffraction by placing a slit as thin as possible on the path of an X-ray beam as punctual as possible. There were two goals to these studies, which were initiated by Fomm [FOM 96]. They consisted, on the one hand, of demonstrating that X-rays are waves and, on the other hand, of measuring their wavelength.

Wind and Haga [HAG 99, HAG 03, WIN 99, WIN 01] thus presented their first observations of Fresnel fringes obtained with X-rays. By measuring the space between these fringes, they were able to quantitatively estimate the wavelength of X-rays. The value they found was in the range of one angström. The results of these studies were disputed by Walter and Pohl [WAL 02, WAL 08, WAL 09]. They examined the works of their colleagues and conducted new experiments, by using slits a few micrometers wide placed, roughly one meter away from the photographic plate. They did not observe any fringes in the photographs they obtained and concluded that the diffraction effect did not occur. By considering, however, that the