A voltage applied between the two faces of the semiconductor enables the user to measure the electric charge, which is proportional to the energy of the incident X photons. A diagram of such a device is shown in Figure 2.24.

The main advantage of this type of detector is its energy resolution. This resolution is set by the energy required for creating an electron-hole pair and, in this case, is close to 3.5 eV. Therefore, it is used for studies in energy dispersion which are rarely applied in diffraction and that will not be described here. We will simply point out that this type of detector is showing interesting developments in the field of X-ray diffraction, but these are still nothing more than prospects [HON 92, OTT 97].
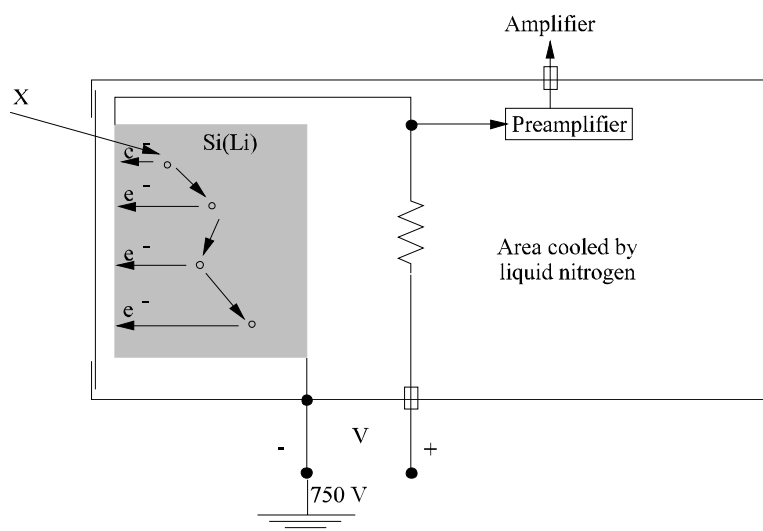

Figure 2.24. *Diagram of how a semiconductor detector works*

2.2. Diffractometers designed for the study of powdered or bulk polycrystalline samples

Nowadays, most diffractometers are modern versions of devices designed during the first quarter of the 20th century. We saw in the introduction of this book that the first diffraction measurements on polycrystalline samples were conducted in 1916, only four years after the discovery of diffraction by single crystals. The first three devices which we will describe in this part of the book were designed between 1916 and 1920, whereas the other two date back to only 10 years ago for the first and two or three years for the second.

Aside from their field of application, the essential difference between these diffractometers is their geometric layout [GUI 05]. In particular, the relative positions of the source, of the sample-holder and of the detector are different. Therefore, the description of these devices will rely essentially on geometric considerations. One of the most significant consequences of choosing a particular geometric configuration is the angular resolution of the device. Therefore, the description of these devices will be illustrated by measurements which make it possible to evaluate this essential feature.

Generally speaking, the objective of the following detailed descriptions is to enable researchers or engineers who are implementing X-ray diffraction for the characterization of polycrystalline samples to choose the device best adapted to their needs. It goes without saying that no device is able to make every type of measurement, hence the need to know their advantages and drawbacks.

2.2.1. *The Debye-Scherrer and Hull diffractometer*

This was the device used in 1916 by Debye and Scherrer [DEB 16] in Germany, and later in 1917 by Hull [HUL 17a, HUL 17b] in the USA, to conduct the first diffraction experiments on polycrystalline samples. A schematic view of the geometrical arrangement of this device is shown in Figure 2.25. The sample is irradiated with an X-ray beam produced by a Coolidge tube. The diffracted beams are collected by using a cylindrical detector placed so as to have the sample on its axis.
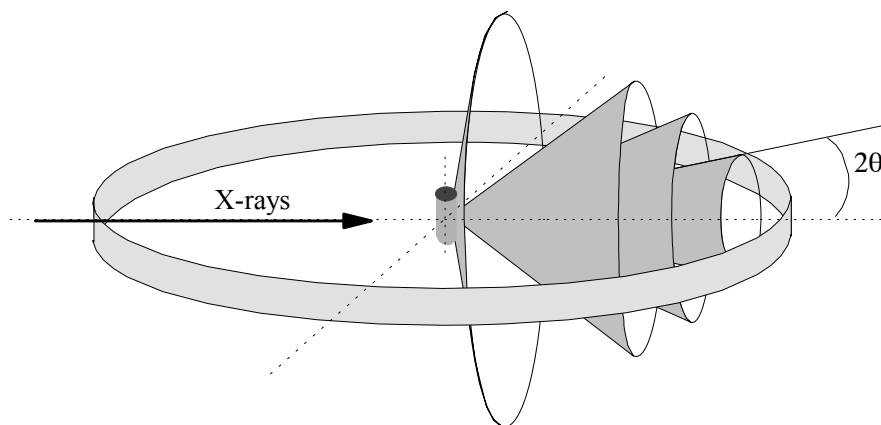

Figure 2.25. *Geometric arrangement of the Debye-Scherrer and Hull diffractometer*

2.2.1.1. *The traditional Debye-Scherrer and Hull diffractometer*

The X-rays emitted by the Coolidge tube penetrate the cylindrical chamber on the axis of which is placed the sample. An imprint of the diffracted beams is produced using a film placed on the inside of the chamber. The intersection of the diffraction cones and the cylinder gives diffraction arcs with a curvature that depends on the angle. These arcs become lines when $2\theta = 180°$ and their curvature is reversed beyond that.

In order to obtain a relatively fine beam, to limit the width of the arcs, a collimator is added to define the beam's geometry. However, the beam has to remain wide enough to ensure a high enough intensity. After going through the sample, the transmitted (non-diffracted) beam is still very intense and widely scattered by the air present inside the chamber. This effect significantly darkens the film in the vicinity of the direct beam and can prevent certain arcs with low diffraction angles from being seen. This effect can be virtually eliminated by adding a beam stop as close as possible to the sample, which absorbs most of the transmitted beam immediately after it exits the sample, thus significantly containing the effects of this scattering.

Two sample holders can be considered, but they must always be made of glass so as not to diffract the X-rays.

Fiberglass

In this case, the sample holder is made of fiberglass, which is as thin as possible, on which the powder we wish to study is deposited and glued using a thin layer of grease.

This method, while relatively simple, has a drawback. The powder located on the edges of the fiber cannot be placed in exactly the center of the device, which widens the diffraction arcs.

Capillary

This time, the powder sample is placed inside a glass tube with very thin sides. The major problem of this sample holder is absorption, since the X-ray beam must go through the tube's walls and therefore be partially absorbed. Therefore, the capillary is made out of low absorbing material, in practice Lindemann glass or silica.

Regardless of whether the sample holder is a fiber or a capillary, it has to be placed in the center of the chamber. Therefore, the stand made for the sample holder is built on a moving axis that can be adjusted using a system of screws and springs. This adjustment must imperatively be made before each experiment.

In both cases, the quantity of material used is very small, since the analysis is transmission-based, making it important to limit the absorption by the sample. In order to prevent effects caused by too small a number of grains, the stand for the sample holder can rotate, so that each grain can be, in turn, placed in the Bragg position for different families of planes.

The beam originating from the X-ray tube is polychromatic. In order to select the appropriate wavelength, the Debye-Scherrer and Hull devices are usually equipped with filters. The use of monochromators is a possibility, but the intensity of the diffracted beams would be too low and the exposure times too long. The $K_{\alpha 1}$-$K_{\alpha 2}$ doublet cannot be separated with filters, which constitutes one of the limitations of this type of device. A schematic view of a traditional Debye-Scherrer and Hull diffractometer is shown in Figure 2.26.
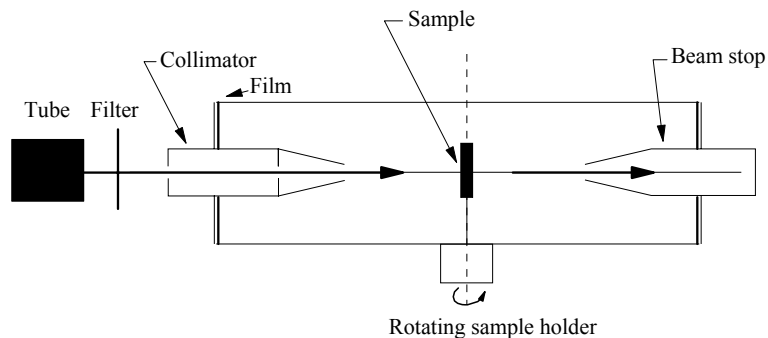

Figure 2.26. *Traditional Debye-Scherrer and Hull diffractometer*

Figure 2.27 shows a film obtained for a sample of magnesium oxide.

Each of the arcs corresponds to a family of crystal planes with an interplanar distance that can be inferred from Bragg's law and a measurement of the diffraction angle. In order to make the interpretation simpler, the radius of the chamber is such that a length of 180 mm on the film is equivalent to an angle of 180° (the radius has to be equal to 57.3 mm).

Figure 2.27. *Film recorded in a Debye-Scherer and Hull diffractometer with a sample of zinc oxide*

Each diffraction cone leads to two arcs with symmetric positions with respect to the center of the film, which is defined by the direct beam. We saw that the half opening angles of the cones is equal to 2θ and, since the distance between two arcs corresponds to a single cone, a direct reading gives the angle 4θ.

These traditional Debye-Scherrer diffractometers are no longer used today. Their geometry is such that the beams diffracted by the sample are divergent, or at least do not converge on the detector film. This intrinsic situation causes the diffraction arcs that are detected to widen, hence causing a poor angular resolution. We will see later on that other configurations make it possible to detect diffracted beams where they converge, thus increasing the angular resolution. Furthermore, the detection of diffracted beams in these systems was achieved with photographic film. This makes it more difficult to process the data with a computer. These two elements caused these systems to gradually disappear. However, at the beginning of the 1980s, the arrival of position sensitive gas detectors led to a renewed interest in this type of system. New devices were designed and even though they are distant relatives of the ones used in the early 20th century by Debye, Scherrer and Hull, they are of the same kind in the sense that the sample is in the center of the detection circle [SHI 86].

2.2.1.2. *The modern Debye-Scherrer and Hill diffractometer: use of position sensitive detectors*

Strictly speaking, photographic film is a position sensitive detector but, as we have already mentioned, the resulting signal is not directly digital. This is why modern Debye-Scherrer and Hull diffractometers combine a beam originating from a plane or curved monochromator with a one-dimensional position sensitive detector, giving the user a direct reading of the diffraction signal and with the sample placed in its center. In the first part of this chapter, we described the different types of detectors, and saw that, today, there are position sensitive gas or solid detectors that use an imaging plate. The latter are of much more recent design than the former, so the modern Debye-Scherrer and Hull systems were developed by implementing the concept of curved position sensitive gas detectors. Additionally, this type of gas detector requires the sample to be placed in the center of the detector[4], since the beams diffracted by the sample have to travel the same distance inside the detector regardless of what diffraction angle is considered. Variations of this distance would modify the measurements of the diffracted intensity. Hence the use of curved position sensitive gas detector requires a Debye-Scherrer and Hull geometry. As we have already said, the use of one-dimensional imaging plate

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4 Some authors [ORT 78; WOL 81; WOL 83] thought of placing the sample on the detection circle, i.e. on the circle defined by the curved detector. This configuration was tested with a detector with a small radius; however, the intensity measurements were not accurate and it would be necessary to include corrections in this case. It would seem that no one until now has suggested a satisfactory method.

detectors is much more recent. We will give a few details about this at the end of this section.

2.2.1.2.1. The traditional modern Debye-Scherrer and Hull diffractometer: cylindrical sample

Figure 2.28 shows a schematic drawing of a Debye-Scherrer device equipped with a curved position sensitive detector.
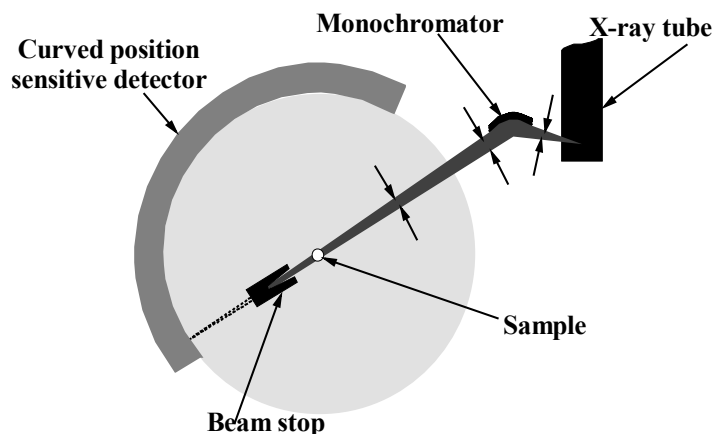

Figure 2.28. *Debye-Scherrer diffractometer equipped with a position sensitive detector*

The sample is irradiated with an incident monochromatic beam originating from a Guinier type, curved crystal monochromator. Due to the crystal's curvature being set, the front and rear focal distances are fixed and the beam's section is defined by the slit located between the tube and the monochromator. The two slits placed beyond the monochromator are oriented in the direction defined by the monochromator's diffraction angle, making it possible to actually select the source's $K_{\alpha 1}$ radiation. This matter will be discussed in great detail later on when we discuss the Bragg-Brentano diffractometers.

The sample is a fine cylinder usually comprised of a capillary filled with the powder we wish to study. It can also be made of a thin wire, particularly when the material we wish to study is a metal. In any case, this sample is placed in the center of a curved, position sensitive gas detector used to simultaneously detect all of the diffracted beams. We saw before that when these gas detectors are irradiated with X photons, the gas is ionized and a local avalanche effect takes place which leads to the ionization of the neighboring atoms. The size of this ionized zone depends on

the operating conditions of the detector. Some detectors operate in proportional conditions, others in intermediate conditions between the proportional conditions and the Geiger-Müller and they are referred to as the "streamer conditions" [ALE 80; ATA 82; BAL 83]. At any rate, the linear dimension of the ionized zone can be considered to be in the order of 150 μm. The detector's[5] angular resolution is directly related to its radius and can therefore be estimated from this value of 150 μm. It would seem that the radius must be as large as possible. However, we should point out that this increases the length of the delay line, and thus significantly complicates the design of such a detector. The detectors currently available have radii between 250 and 500 mm. Due to the absorption by the air surrounding the sample, the increase in the sample-detector distance causes a significant decrease in the measured intensity. We could of course consider designing systems where the sample is placed in the center of a chamber with a crude vacuum, but this considerably complicates the design of the equipment and increases its cost.
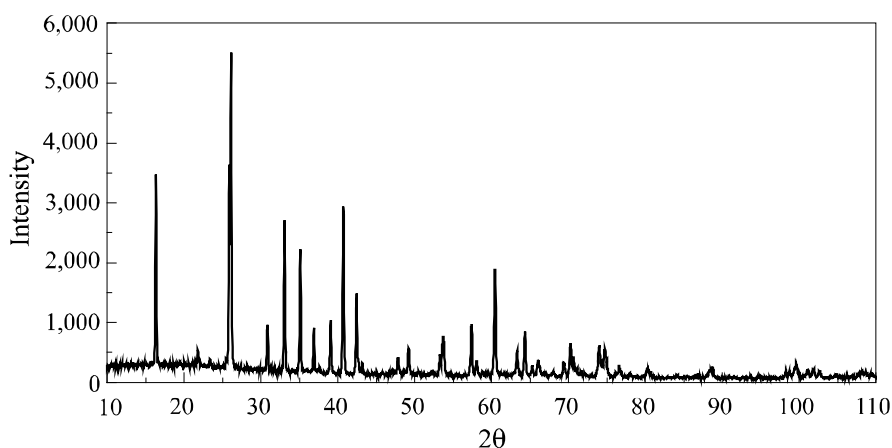

Figure 2.29. *Diffraction pattern obtained using a Debye-Scherrer and Hull device equipped with a curved position sensitive gas detector*

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5 A diffractometer's angular resolution is one of its essential features. However, it depends not only on the resolution of each of the elements that comprise it, but also on the device's general configuration, in particular on the relative positions of its various elements. What we are discussing here is the detector's resolution, not to be confused with the device's global resolution. For example, it is quite odd to say [PEC 03] that the angular resolution of those diffractometers including such position sensitive detectors is not good since that resolution depends on the configuration. We will show later on that high resolution devices can be produced with this type of detector, for example by optimizing the incident beam's geometry.
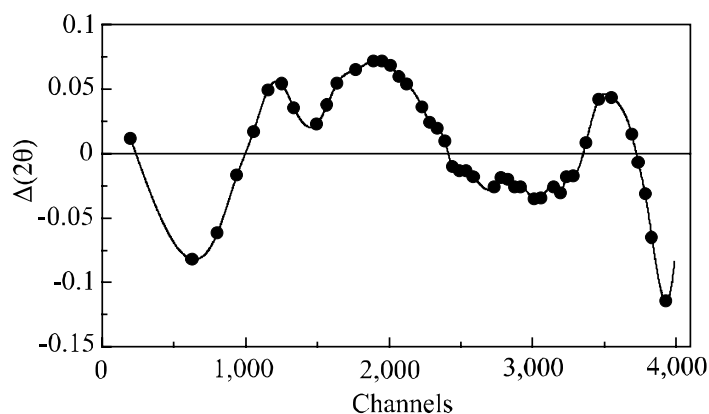
The detected signal is then plotted in a diagram showing the evolution of the diffracted intensity according to the diffraction angle (see Figure 2.29). The main advantage of this type of system is very clear. All of the diffracted beams are collected simultaneously. We will see other systems later on, in particular the Bragg-Brentano diffractometer, where the detection must be intrinsically punctual. The acquisition time of a diagram is in that case longer. In practice, these Debye-Scherrer and Hull diffractometers make it possible to produce diffraction patterns in a few minutes or sometimes a few seconds [YAM 92].

The arrival on the market of these curved position sensitive gas detectors stirred new enthusiasm for this configuration. Several laboratories, among them the Nantes Institute for Materials [DEN 93, EVA 93], have dedicated their research to study the characteristics and the quality of diffraction patterns produced using this kind of device. With these diffractometers designed for fine cylindrical samples (capillaries), the equipment's angular resolution directly depends on the diameter of the sample, since that is the dimension that determines the incident beam's useful part. In the conventional configuration, which is the one studied by Evain [EVA 93], the detector's radius is 250 mm. In this case, if we use a capillary that is 0.5 mm in diameter, the peak widths vary between 0.08° and 0.16° when the diffraction angle changes from 10° to 120°. This study shows that the angular resolution of these devices is high, but not as good as the one obtained with a Bragg-Brentano device in its high resolution configuration, which will be described later on.
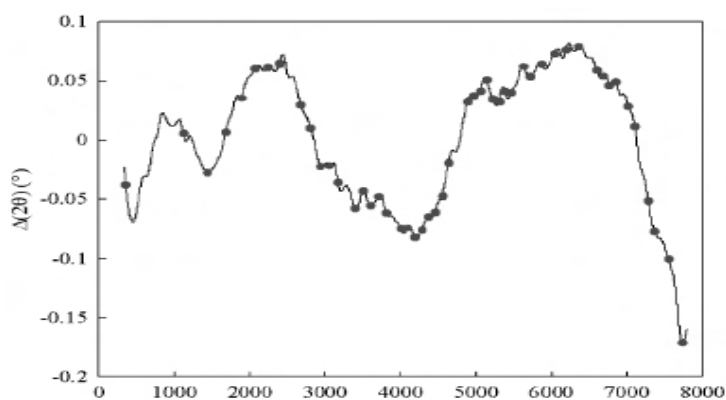
These position sensitive gas detectors are divided into different channels and each intensity is specified with its channel number. Therefore, the pattern obtained after the acquisition gives the diffracted intensity according to the channel number. The relation between the channel number and the angle is not strictly linear, straying from the straight line by about a tenth of a degree (see Figure 2.30). These significant differences constitute one of the major weaknesses of these detectors. We will see, however, that angular calibration can help solve this problem. However, we should point out that the quality of this calibration, which is obtained experimentally, determines the accuracy of the diffraction angle measurements. Since the early 1980s, three methods have been found to perform the angular calibration on these systems.

The first method consists of placing in front of the detector window a sheet of metal pierced at regular intervals with very thin holes. The detector is then irradiated using an isotropic radiation source (a radioactive source, or fluorescent radiation). In each point corresponding to the holes, a peak is observed. Since the holes are regularly spaced out, it is possible to draw the link between the channel and angle numbers [STA 92]. This method assumes that the sheet is perfectly cylindrical and that it has the same center as the detector, a condition that is difficult to meet.

The second method consists of recording a diffraction diagram for a perfectly well-known sample [EVA 93, MAS 96a]. The positions of the diffraction peaks, along with the corresponding channels, are matched with the values of the diffraction angles associated with the characteristic interplanar distances of the control sample. The result is the relation between the channel and the angle number.

(a) Illustration of the straying from linearity. The dots correspond to the measurements conducted on a sample of $Na_2Ca_3Al_2F_{14}$ [COU 88]

(b) Comparison of several calibration methods [MAS 05]. The black dots correspond to measurements conducted on a standard sample of $Na_2Ca_3Al_2F_{14}$. The full line is obtained by calibrating the detector with a rotation in front of the direct beam, with measurements conducted every 0.5°

Figure 2.30. *Angular calibration of a curved position sensitive detector*

A third method consists of turning the detector step by step in front of the direct beam by recording the direct beam at each step [STA 94, MAS 98a , MAS 05]. Since the increment is known, the angular calibration is directly obtained. As Figure 2.30b shows, this last method is the most effective, but it requires to be able to turn the detector with an accuracy in the range of a thousandth of a degree. The system can be equipped with a motorized rotation, and the calibration according to this method can then be performed automatically.

Generally speaking, the most commonly used method is the second one. When this calibration is properly done, it enables the user to perform measurements of diffraction diagrams with a high angular accuracy [DEN 93, MAS 96a].

As we have already said, systems equipped with position sensitive gas detectors can produce diagrams with very short acquisition times. In addition to this, the measurement of the diffracted intensity is achieved in every point of the diagram simultaneously and therefore if the sample changes due to the effect of an outside solicitation, the entire diagram is modified. This characteristic feature of systems using position sensitive detectors makes Debye-Scherre and Hull systems very good candidates to follow the *in situ* evolution of materials according to one or several outside constraints.
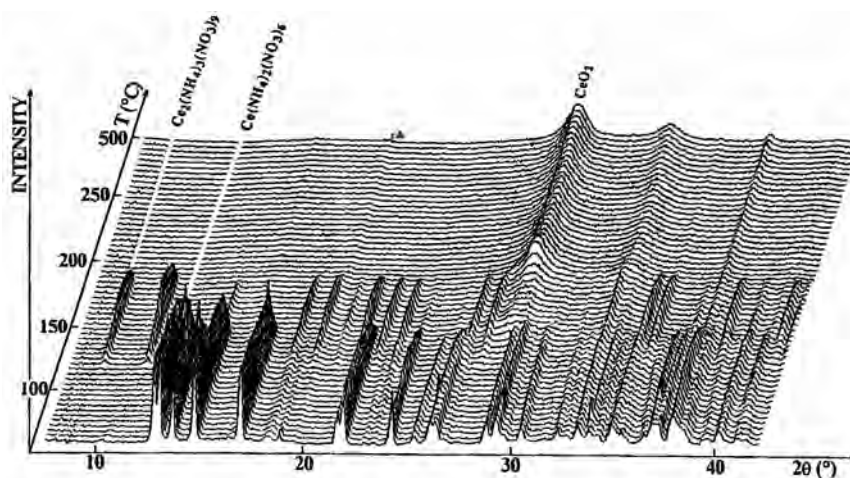

Figure 2.31. *Study of the crystallization of cerium oxide using a thermodiffraction system equipped with a curved position sensitive detector [BEN 96]*

This characteristic was used, for example, to produce diffractometers designed to track the evolution of a sample according to the temperature. Louër and his colleagues studied the structural transformations of oxide precursors using a system equipped with an oven in which the sample was placed [AUF 90, BEN 93, GUI 95, BEN 96]. An example of this type of study is shown in Figure 2.31 where the evolution of a cerium oxide precursor can be observed, showing in particular the presence of an intermediate phase. The same approach was used by other authors to study, for example, the dehydration of zeolites [STA 92, STA 94] or also to simultaneously measure, according to the temperature, the evolution of X absorption spectra (EXAFS) and of diffraction patterns [SAN 93, DEN 95].

The maximum number of photons that a gas detector can measure per unit of time depends on the operating conditions of this detector, but is nonetheless relatively limited compared with the possibilities offered by solid detectors. This limitation can be bothersome when the incident intensity is very high, such as when using a synchrotron radiation source or when it is important to precisely measure the diffracted intensity over a large number of orders of magnitude[6]. In the past few years, several authors have suggested creating Debye-Scherrer and Hull diffractometers which use one-dimensional "image plate" detectors [SAB 95, BAR 92, O'CO 97, NIS 01, TAK 02, KNA 04]. These systems were designed to be used with synchrotron sources and there are currently no manufacturers selling this type of equipment to laboratories. We will see later on that this type of detector can be used to create Seemann-Bohlin systems, where the sample is placed on the detection circle. This configuration, which uses a convergent X-ray beam, makes it possible to obtain patterns with a high angular resolution. Therefore, it would seem more favorable for laboratory experiments than the Debye-Scherrer and Hull configuration. Naturally, this question does not come into consideration for synchrotron radiation sources, since in that case the incident beam is parallel.

The use of a sample holder requires the sample to be reduced to a fine powder. This condition is not a problem when determining, for example, the structure of a new phase that has just been synthesized and this type of equipment is used for that purpose by solid state chemists. However, it is sometimes necessary to directly study bulk samples for which grinding could cause phase transitions. In those cases, the sample is a plane object that can be studied with the same diffractometer. Different configurations are then possible, with different paths for diffracted beams and different angular resolutions depending on the relative positions of the various elements included in the apparatus.

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6 This last case occurs, for example, when studying epitaxial thin films. This matter will be discussed in Part 2 of this book.

2.2.1.2.2. Use of plane samples: configuration of the device and angular resolution

Figure 2.32 shows a schematic drawing of a Debye-Scherrer and Hull device devoted to the study of flat plate samples.
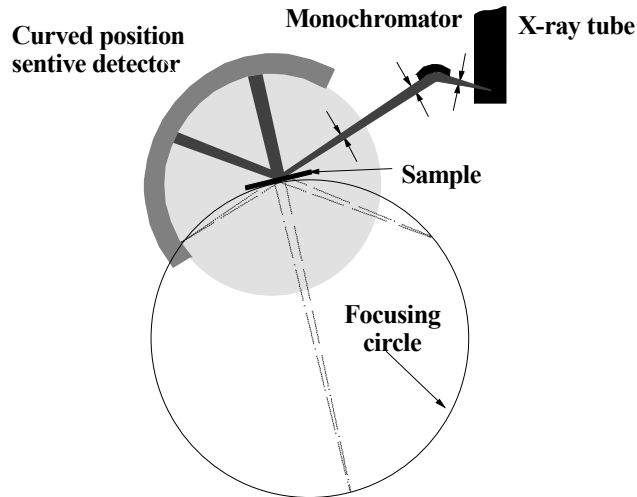

Figure 2.32. *Debye-Scherrer diffractometer with a flat plate sample. Study in reflection*

Each diffraction peak that is observed in the direction 2θ results from all of the X photons diffracted by all of the grains in the Bragg position, for the family of reticular planes corresponding to the distance d, such that $\lambda = 2d \sin \theta$. These X photons are diffracted by all of the grains along the angle θ with respect to the family of planes in question, but the X-ray beam originating from the curved monochromator is convergent (and non-parallel). Therefore, the diffracted X-ray beams are not parallel; in the situation shown in Figure 2.32, the beams that reach the detector are divergent (see Figure 2.33). The locus of convergence of these beams is virtual in this case, since it is located behind the sample. It consists of a circle (the focusing circle) that is tangent to the sample and that passes through the convergence point of the beam originating from the monochromator (see Figure 2.32).
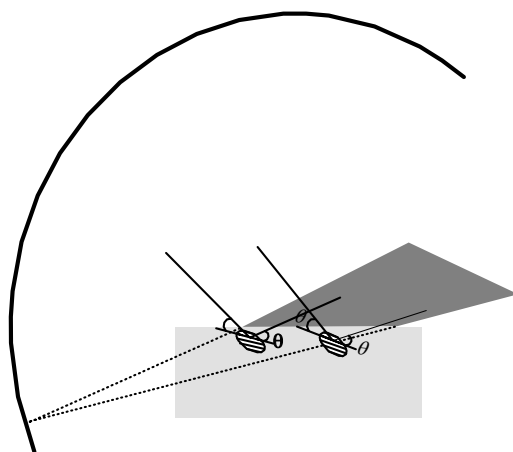
Figure 2.33. *In the configuration shown in Figure 3.31, the beams diffracted for a same angle by different crystals inside the sample are divergent*

Therefore, the configuration shown in Figure 2.32 seems to be unfavorable, since the diffraction peaks are in that case relatively wide. On the other hand, if the convergence point is located in front of the sample, the diffracted beams converge toward the detector (see Figure 2.34).
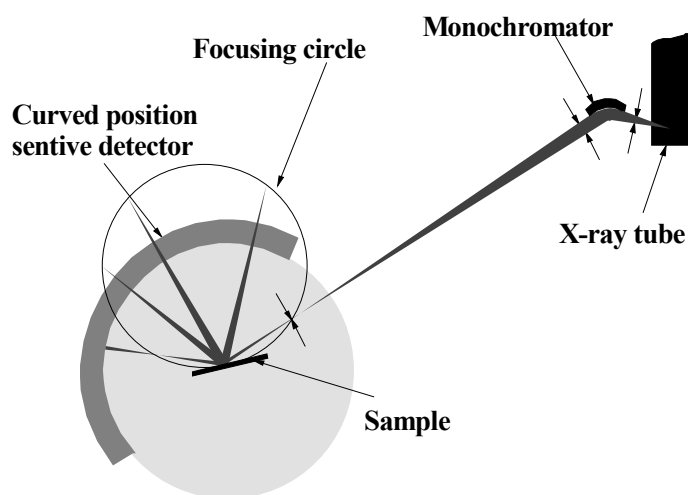

Figure 2.34. *Debye-Scherrer diffractometer with a flat plate sample. Study in reflection with the convergence point of the incident beam in front of the sample*

The reverse situation is observed when the sample is studied in transmission: the diffracted beams are convergent if the focusing point of the direct beam is placed in front of the sample (see Figure 2.35) and otherwise divergent.
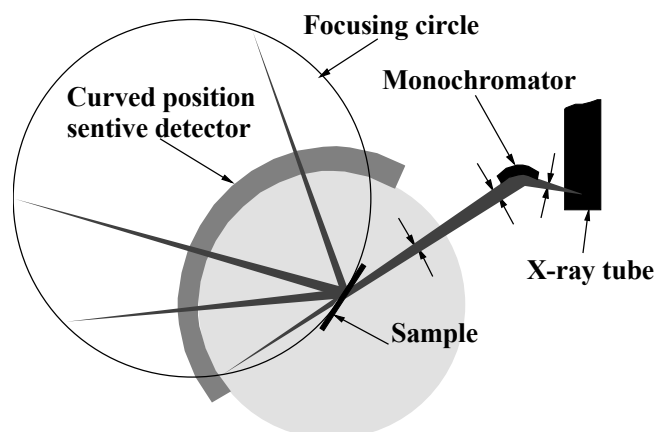

Figure 2.35. *Debye-Scherrer diffractometer with a flat plate sample. Study in transmission with the convergence point of the incident beam behind the sample*

Regardless of which configuration is chosen, the curved position sensitive gas detector cannot be placed on the focusing circle, since in that case, as we mentioned above, the detector's attack angle would vary and therefore the distance traveled by the photons in the gas would depend on the Bragg peak is considered; the intensity measurements would then be inaccurate. The diffracted beams could possibly be convergent, but the observed peaks would remain relatively wide, since the detector is not placed on the focusing circle. Note, however, that if we increase the focal distance behind the monochromator, the beam becomes more and more parallel, which causes the diameter of the focusing circle to increase. Thus, if this focal distance is high enough, the influence of this defocusing effect is small. In practice, these devices are equipped with a monochromator comprising of a quartz or germanium crystal that is curved, so that the back focal distance is close to 1 meter, making the influence of the defocusing effect rather small. Another approach enabling the user to modify the diameter of the focusing circle consists of modifying the incidence angle of the X-ray beam on the sample. We may choose a situation where the incidence angle is equal to the Bragg angle of certain diffraction peaks deemed interesting; this is referred to as diffraction by symmetric reflection, something we will discuss in greater detail later on. The focusing circle is then tangential to the detection circle and as a result, locally, and for a certain angular range, we obtain a high resolution.

The optimum use of a curved detector with a plane sample probably requires a thin parallel incident beam in order to prevent any convergence or divergence effects. Such a beam could be obtained with a plane monochromator comprised of several reflections. This led Dumont [DUM 37], followed by Bartels [BAR 83], to design a monochromator with four reflections on single crystals of germanium. The beam originating from this monochromator is strictly monochromatic and shows an extremely low divergence. We can mention, as an example, the values obtained for a monochromator using four reflections on the planes (220) of the germanium crystal. The resulting spectral dispersion is $\Delta\lambda/\lambda = 1.4 \times 10^{-4}$ and the divergence is $\Delta\theta = 12$ arcseconds. The diagram of a system including such a monochromator associated with a curved detector is shown in Figure 2.36 [GUI 96, MAS 98a, BOU 02a]. Naturally, this type of monochromator greatly reduces the intensity of the beam hitting the sample, but causes a very high increase in resolution.
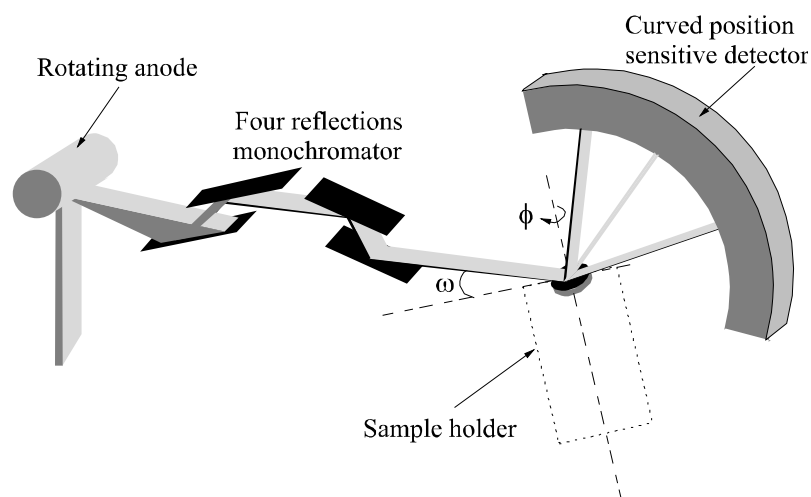

Figure 2.36. *Diffractometer associating a position sensitive detector with a flat plate sample and a parallel beam*

In order to illustrate this result, we realized two diffraction patterns using a sample with a low crystal symmetry, hence the large number of peaks. One of the patterns was recorded with a diffractometer using a convergent beam and corresponding to the setup described in Figure 2.32. The other pattern was obtained using the diffractometer shown in Figure 2.36. The sample that was chosen is a monoclinic zirconia powder used in an international structure refinement test [HIL 94] performed under the authority of the International Union of Crystallography.

The results of these measurements are shown in Figure 2.37. Note how the use of a strictly parallel beam can greatly improve the diffractometer's angular resolution. As we will see later on, the resolution of this diffractometer is equivalent to that obtained with Bragg-Brentano diffractometers in the high resolution configuration.
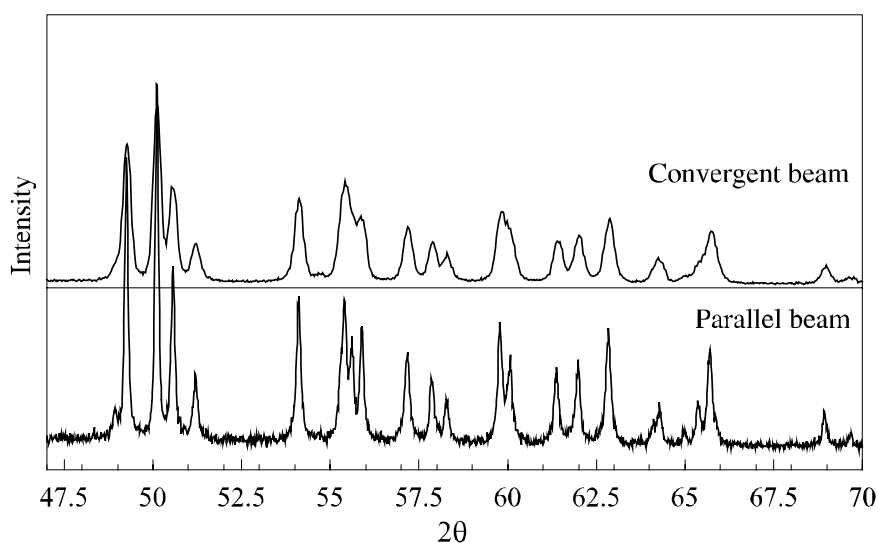

Figure 2.37. *Influence of the diffractometer's geometry on the angular resolution, illustrated by diffraction patterns of monoclinic zirconia*

2.2.2. *Focusing diffractometers: Seeman and Bohlin diffractometers*

2.2.2.1. *Principle*

A few years after the first experiments led by Debye, Scherrer and Hull, Seemann [SEE 19] and Bohlin [BOH 20] thought of an X-ray diffraction apparatus for polycrystalline samples that would detect where they converge the beams diffracted by the crystals in the Bragg position. The corresponding configuration is shown in Figure 2.38.

The X-rays produced by the source, placed in S, are divergent. They hit a curved sample and, for given family of planes corresponding to a certain diffraction angle, all of the beams diffracted by the crystals for which that family of planes is in the Bragg position converge to a point F, located on the circle that passes through S and to which the sample is tangent.
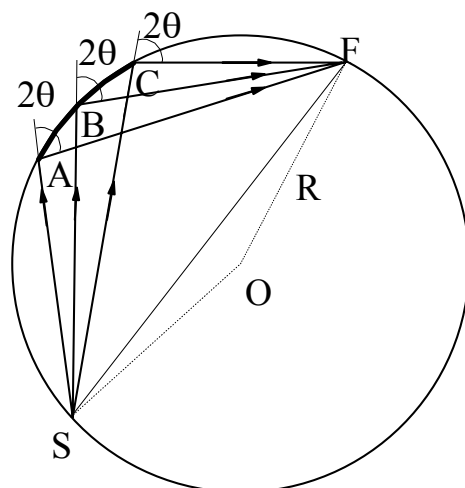
Figure 2.38. *Geometric arrangement of a Seemann-Bohlin diffractometer*

This description corresponds to a plane projection of the apparatus. In a three-dimensional perspective, all of the diffracted beams converge to F if and only if the sample is placed on a section of the torus generated by the rotation of the arc AC around the line SF and, of course, if the source is punctual.

In practice, this condition is not met, that is, the source is linear and is equivalent to a line segment perpendicular to the projection, essentially so as to have a strong enough intensity. The sample is then comprised of a portion of a cylinder and the focusing locus is a line segment parallel to the source.

2.2.2.2. *The different configurations*

2.2.2.2.1. Use of a curved monochromator (Guinier chamber) [GUI 37, GUI 39, WOL 48]

Following the works of Seemann and Bohlin, these systems were improved by several authors [GUI 37, GUI 39, WOL 48, HAG 69], the first among them being Guinier, who suggested including a curved monochromator crystal [GUI 37]. The beam's optical path then corresponds to the one shown in Figure 2.39. This is sometimes referred to as the "Guinier chamber" (or also Guinier-de Wolf or Guinier-Hägg). The word "chamber", i.e. to describe a diffractometer, comes from the fact that the detector used was a piece of photographic film. Of course, this feature is not specific to the geometric configuration in question. We will see in the following sections that there are Seemann-Bohlin diffractometers which use other

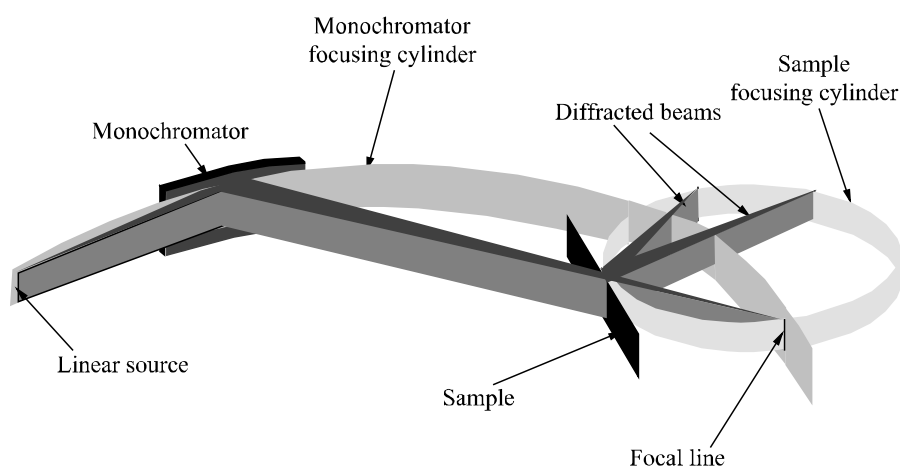kinds of detectors. Therefore, we will be using the word "diffractometer" rather than "chamber".

Figure 2.39. *The Guinier diffractometer*

A Guinier monochromator can separate the $K_{\alpha1}$-$K_{\alpha2}$ doublet. However, there are two possible configurations. Consider a beam with a certain wavelength dispersion headed for the monochromator. In order for a beam with wavelength λ arriving toward the monochromator to be diffracted, it has to be at an angle θ_λ with crystal planes parallel to which the monochromator is cut. If we consider photons with wavelength $\lambda + \Delta\lambda$, they will be diffracted by the monochromator only if they reach it at an angle $\theta_{\lambda + \Delta\lambda}$. Therefore, it is necessary that they originate from a slightly different area of the source (see Figure 2.40a). On this condition, these photons with wavelength $\lambda + \Delta\lambda$ are diffracted in a direction defined by the angle $\theta_{\lambda + \Delta\lambda}$. This means that the diffracted photons with wavelengths λ or $\lambda + \Delta\lambda$ will take different directions. The sample has the same effect as the monochromator and a given family of planes will diffract these two beams in slightly different directions. The two possible configurations are shown in Figure 2.40.

S configuration (subtraction)

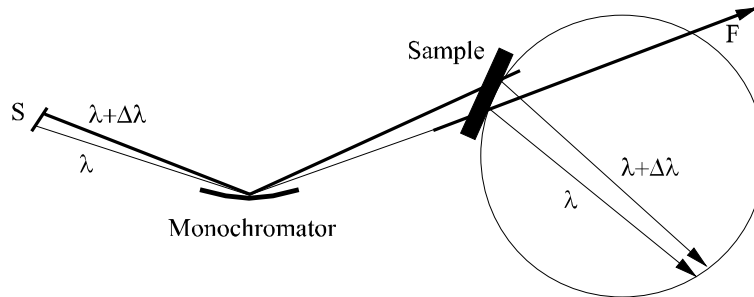The two effects are subtracted and the diffraction on the sample tends to bring the two beams closer together.

Figure 2.40a. *S configuration of a Seemann-Bohlin diffractometer*

O configuration (addition)

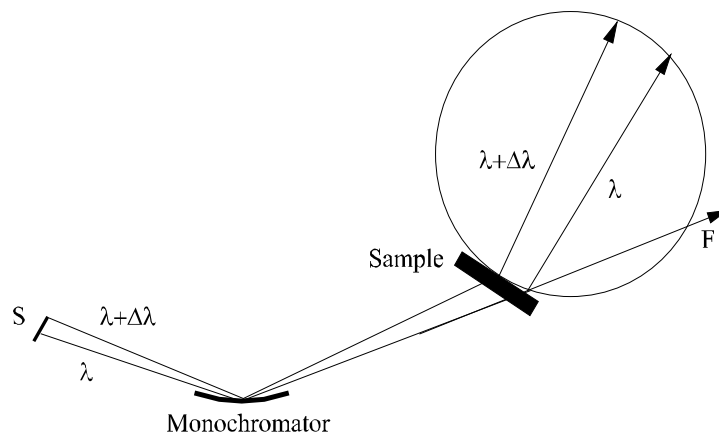The beams diffracted by the sample are more separated than they were before the diffraction.

Figure 2.40b. *O configuration of Seemann-Bohlin diffractometer*

Current Seemann-Bohlin diffractometers can be used in either configuration. The S configuration has a better angular resolution.

2.2.2.2.2. Transmission, reflection; symmetric, dissymmetric

These diffractometers can be used in various configurations. All of the possibilities are shown in Figure 2.41.
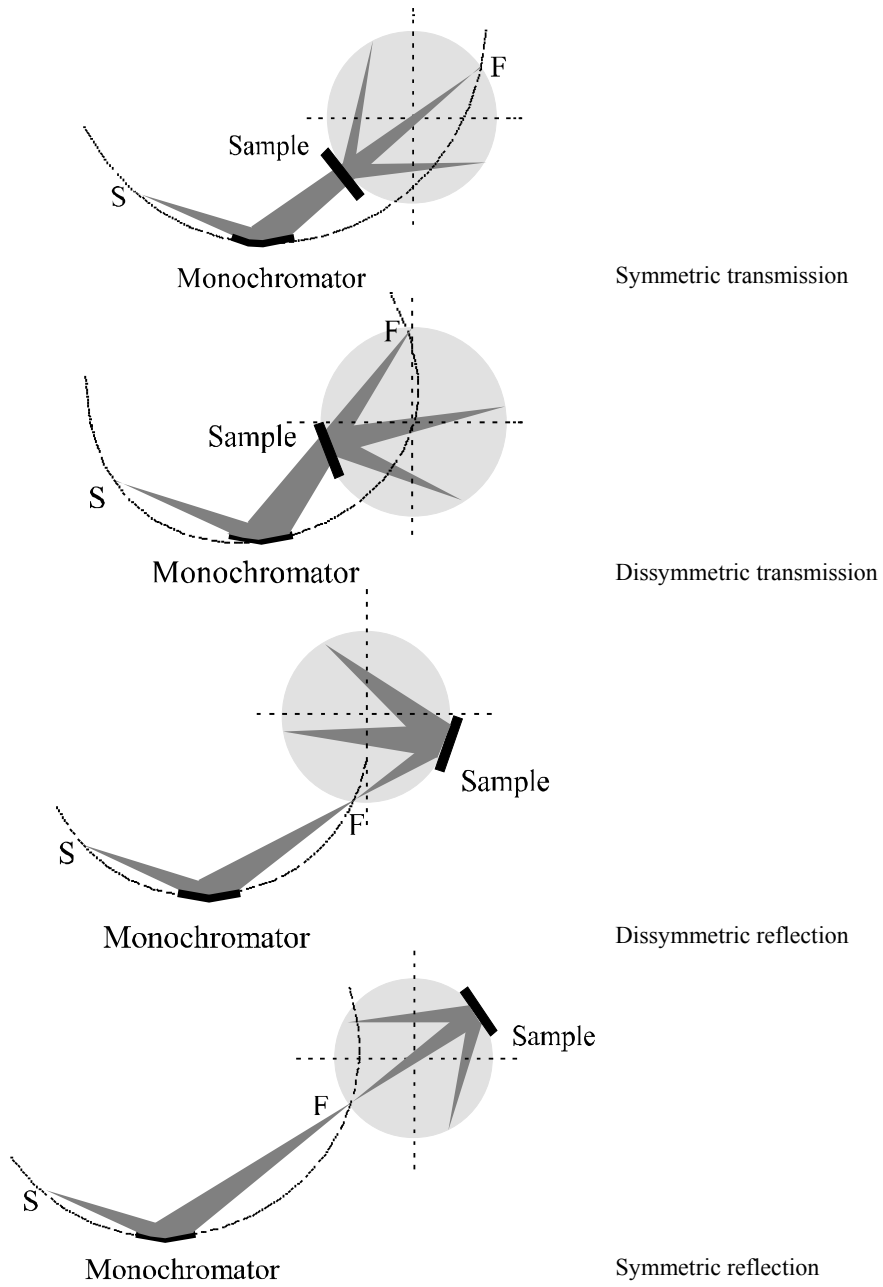
Figure 2.41. *Use in transmission or in reflection*

Note, however, that the choice of one configuration or another imposes an angular area on the measurement. Generally speaking, the use of the system in reflection makes it impossible to measure peaks at low angles, the angle θ must be higher than 37°. Due to this very restrictive condition, Seemann-Bohlin diffractometers are used in transmission most of the time. The reflection configuration is only used when the measurements involve peaks with high angles. This can occur for very precise measurements of cell parameters for purposes of evaluating the rate of homogenous strains.

Hofmann and Jagodzinski [HOF 55] designed a double chamber system, one used in transmission and the other in reflection. The angular range covered by this design is of 0 to 45° for the first chamber and 45 to 90° for the second. The two combined enable the user to make measurements from 0 to 90°. This configuration, however, is rarely used.
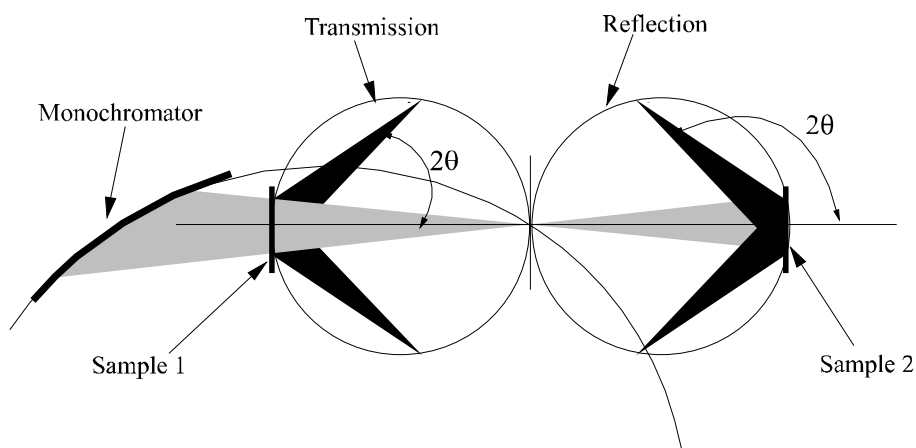

Figure 2.42. *Double Guinier chamber*

2.2.2.2.3. Simultaneous observation of several samples

Some devices [WOL 48] enable the user to study several samples simultaneously. The different powders are placed on top of each other and diffract different portions of the beam. The resulting film looks like the one shown in Figure 2.43 [KLU 74].
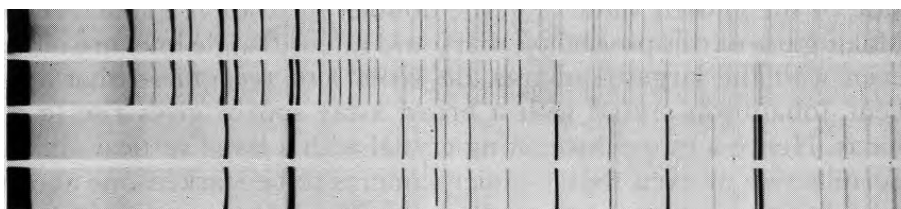
Figure 2.43. *Film obtained from the simultaneous study of several samples*

Guinier devices are diffractometers with a very good angular resolution. However, the use of photographic films as detectors greatly lessens their appeal, since most modern studies require a digital signal that can directly be processed by a computer. There are two different methods for solving this problem.

2.2.2.2.4. Use of an imaging plate detector

Guinier chambers with imaging plate detectors started appearing in the late 1990s [STA 00]. The active material is deposited on a flexible polymer holder, producing a detector, which is simply placed where the photographic film would have been. The signal can be read very quickly because of a lazer source integrated in the diffractometer. This type of device, sold by the Huber company, is still very recent. It seems quite efficient and can produce diffractograms which have a good angular resolution with very short exposure times (a few minutes). However, as we have mentioned before, these detectors show a certain remanence that lessens their appeal.

2.2.2.2.5. Use of a punctual detector: goniometric setup

For many years, another method has been used to directly produce a digital signal using a Seemann-Bohlin diffractometer. Traditional film is replaced with a punctual detector moving along the focusing circle [WAS 53]. Usually, scintillation detectors or proportional gas detectors are used. The detector's movement can be either continuous or incremental.
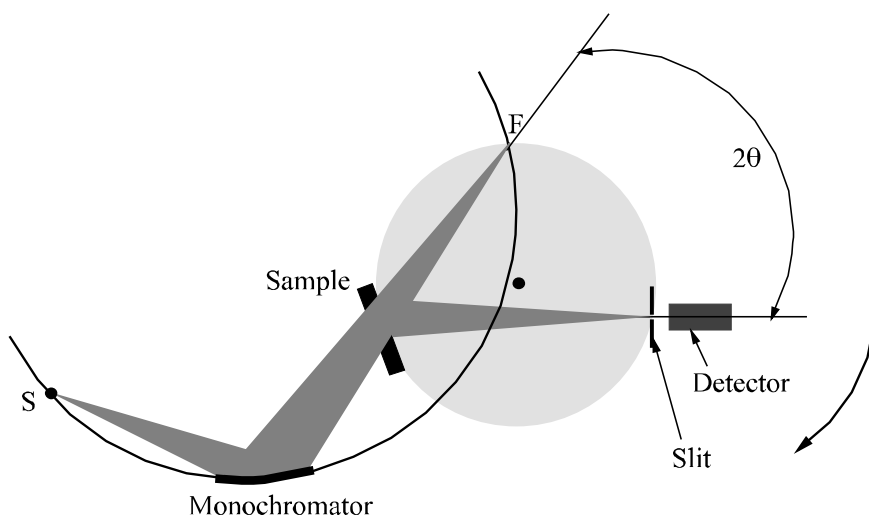
Figure 2.44. *Seemann-Bohlin device equipped with a punctual detector*

These diffractometers were described in detail by Parrish and Mack [PAR 67, MAC 67], and even though they have been available on the market for 40 years, they are only rarely used. They show a high angular resolution but are particularly difficult to adjust. The value of the diffraction angle 2θ is directly given by the detector's position on the focusing circle. Therefore, precisely determining this angle requires the focusing point of the incident beam originating from the monochromator to exactly coincide with the angular zero. In addition, other authors [MAC 67, SPE 95] have noted that any movement of the sample along the radius has a strong influence on the measured position of the diffraction peaks. Hence, it is important that the sample is exactly tangent to the focusing circle.

2.2.3. *Bragg-Brentano diffractometers*

2.2.3.1. *Principle*

Seemann-Bohlin devices which have already been described (see Figure 2.38) are such that the diffracted beams converge to the focusing circle, the diameter of which is constant, thus causing the sample-detector distance to vary with the diffraction angle.
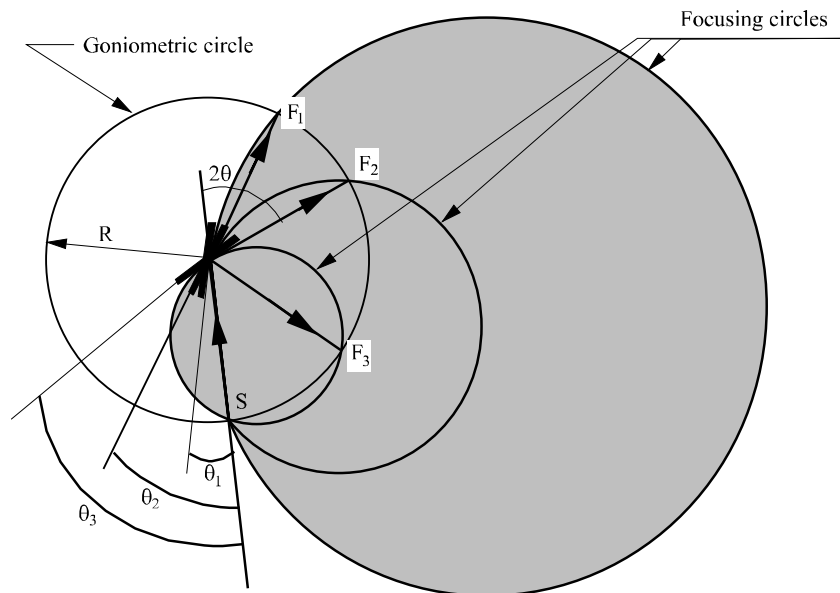
Figure 2.45. *Schematic drawing of the principle of the Bragg-Brentano diffractometer*

Bragg-Brentano diffractometers [BRA 21, BRE 17a, BRE 17b, BRE 46] are approximate focusing systems for which the sample-detector distance is constant for any angle θ. This condition means that the locus of the focusing points is a circle with its center on the sample and passing through S, but it implies that the diameter of the focusing circle changes for each θ. The focusing circles pass through the point S and are always tangent to the sample, which must therefore turn around its center so as to maintain an angle θ with the X-ray beam. Figure 2.45 displays this configuration.

Two types of devices can function this way.

2.2.3.1.1. θ-2θ diffractometers

With this type of device the source does not move, the sample rotates around its axis at a speed ω, whereas the detector is moving at a speed 2ω along the circle, centered on the sample, and referred to as the goniometric circle. The detector, placed in 2θ, measures at every instant the diffraction peaks corresponding to the angle θ.
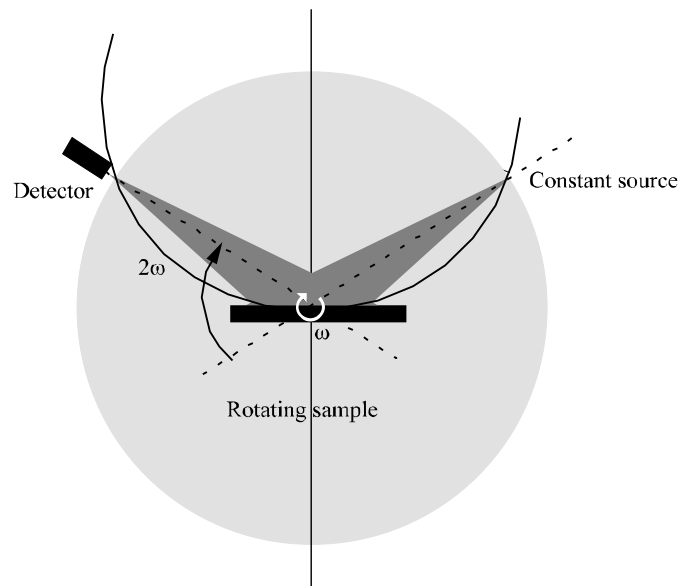
Figure 2.46. *θ-2θ Bragg-Brentano diffractometers*

This is the most common system. However, it has a major drawback: since the sample is rotating, it can sometimes fall, if it is in powder form, when the angle of rotation is too high. The use of this kind of device with a heating sample holder is difficult for the same reason.

It is possible to create a diffractometer based on the same idea, but with a sample that does not move.

2.2.3.1.2. θ-θ diffractometers

With this type of device, the sample does not move. The source and the detector simultaneously move in opposite directions along the goniometric circle at a speed ω.
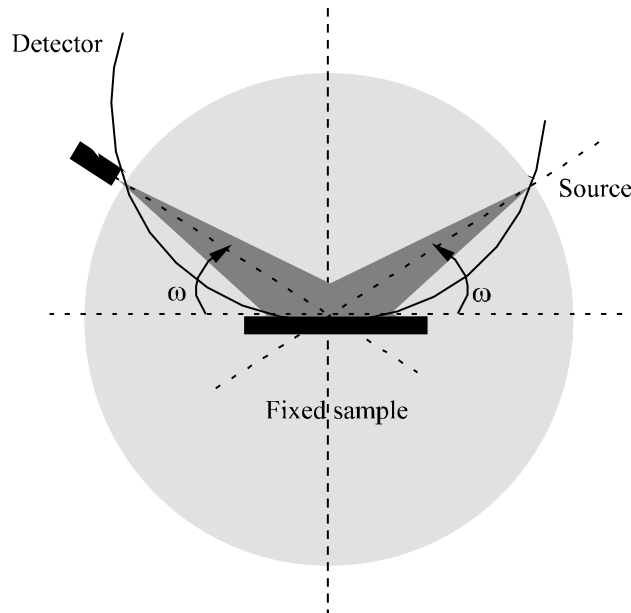
Figure 2.47. *θ-θ Bragg-Brentano diffractometer*

These diffractometers are generally more expensive than the previous ones, since it is difficult to achieve a perfectly controlled movement of the X-ray tube, which is quite heavy.

For both of these two systems, the movements of the different elements can be either continuous or incremental.

2.2.3.2. *Description of the diffractometer; path of the X-ray beams*

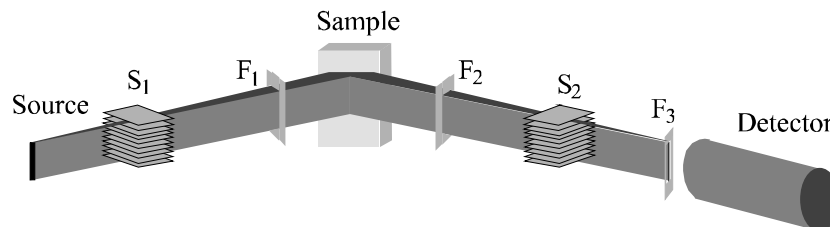A diagram of the X-ray beam's path and of the different elements of the device is shown in Figure 2.47.

Figure 2.48. *Path of the X-ray beams in a Bragg-Brentano diffractometer*

The focal line emits a divergent X-ray beam. A first slit, F_1, makes it possible to limit the incident beam's opening, since it is important, at any diffraction angle, for the area irradiated by the incident beam to be smaller than the sample. Otherwise, the irradiated volume would vary with the angle θ and the relative intensity values would not be specific to the material used. Aside from this particular case, which must be avoided, the volume studied in this type of system is constant for any θ. Note, finally, that the irradiated surface increases when θ decreases. Therefore, when conducting experiments at low diffraction angles, the width of the slit can be decreased. Some devices are equipped with a slit that automatically varies in width with the angle θ. This configuration has its advantages, but the irradiated volume is then no longer constant.
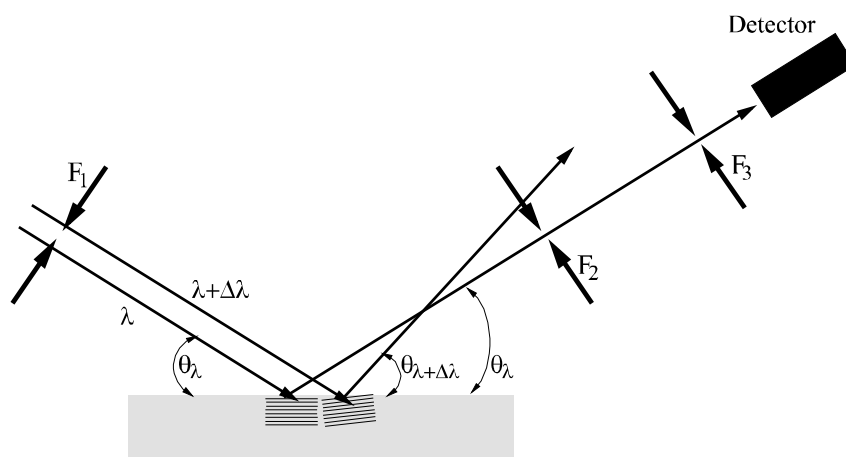

Figure 2.49. *Illustration of how the slits work*

The slits located after the sample (F_2 and F_3) enable the user to select what the detector picks up. As we have already mentioned, in this type of device, the detector is moving along the goniometric circle on which the source is placed and in the center of which the sample is placed. Therefore, the source-sample and sample-detector distances are set and equal to the radius of the circle. This means that the solid angle seen by the detector is entirely determined by the slit F_1, and slits F_2 and F_3 are not necessary in defining the width of the beam as seen by the detector. However, as we have already mentioned, in the case of diffraction by a polycrystalline sample, the incident beam has to be monochromatic. Including a filter or a monochromator associated with slits F_2 and F_3 ensures that only the beams with the chosen wavelength are seen by the detector. The role of these slits is explained in Figure 2.49. In order to make the diagram simpler, the incident beam was assumed to be parallel. In reality it is divergent in Bragg-Brentano systems, but

this does not change the concept. Consider a chosen beam originating from the source and characterized by a wavelength $\lambda + \Delta\lambda$ different from the wavelength λ and a family of planes (hkl) associated with an interplanar distance d_{hkl}. When the sample is irradiated at an angle θ_λ, the crystals for which the family of planes (hkl) is parallel to the surface diffract in a direction defined by the angle θ_λ and the resulting beams hit the detector. The radiation with wavelength $\lambda + \Delta\lambda$ is not diffracted by these crystals, but is diffracted by crystals for which the family of planes (hkl) is slightly disoriented with respect to the sample's surface. The diffraction direction is given by the angle $\theta_{\lambda + \Delta\lambda}$. If slits F_2 and F_3 are positioned in the direction defined by the angle θ_λ, the beams diffracted at an angle $\theta_{\lambda + \Delta\lambda}$ are stopped and not picked up by the detector.

The vertical divergence is limited by two series of slits placed before and after the sample. These slits, referred to as Soller slits [SOL 24], are comprised of parallel plates, regularly spaced out, that divide the beam into several, very slightly divergent beams.

Generally speaking, whatever type of slit is used, they must be made out of highly absorbing materials, and hence of heavy chemical elements. Most of the time, tantalum or molybdenum slits are used.

We have seen that combining different slits can limit the spectral dispersion of the beams picked up by the detector. However, this is only efficient if the incident beams are somewhat monochromatic. Bragg-Brentano systems can be equipped with filters or monochromator crystals. The measurements conducted with the diffractometers are, by nature, sequential, meaning that the acquisition times are directly related to the angular range that is explored, but these times are always longer than those corresponding to overall measurements of the diffraction signal. This characteristic implies that the incident beam that hits the sample has to be as intense as possible. This is why many Bragg-Brentano diffractometers are equipped with filters that make it possible to maintain a significant incident intensity. Figure 2.50 shows a diffraction diagram produced with this type of system equipped with a copper anode source and a nickel filter.

As we have already mentioned, copper's $K_{\alpha 1}$ peak cannot be selected with a filter. Each peak is actually split in two and the angular gap between two peaks corresponding to the same family of planes increases as a function of the diffraction angle.

Adding a monochromator between the source and the sample makes it possible to avoid this problem. However, since the incident intensity is then smaller, the total acquisition time will be longer, often a few days or even up to a week for high resolution patterns.
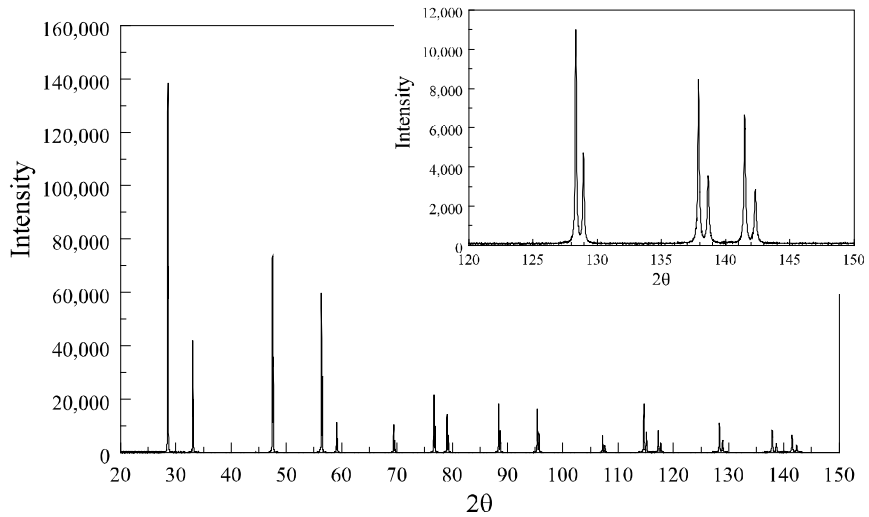
Figure 2.50. *Diffraction pattern of a sample of cerium oxide powder obtained with a Bragg-Brentano diffractometer equipped with a copper anode source and a nickel filter [BAL 04]*

The monochromators must make it possible to irradiate the sample with a divergent beam, which is why, most of the time, curved Guinier monochromators are used. They are made out of quartz or, out of germanium. A diagram of the corresponding set-up is shown in Figure 2.51. The pattern obtained with this device using the same sample as in Figure 2.50 is shown in Figure 2.52.
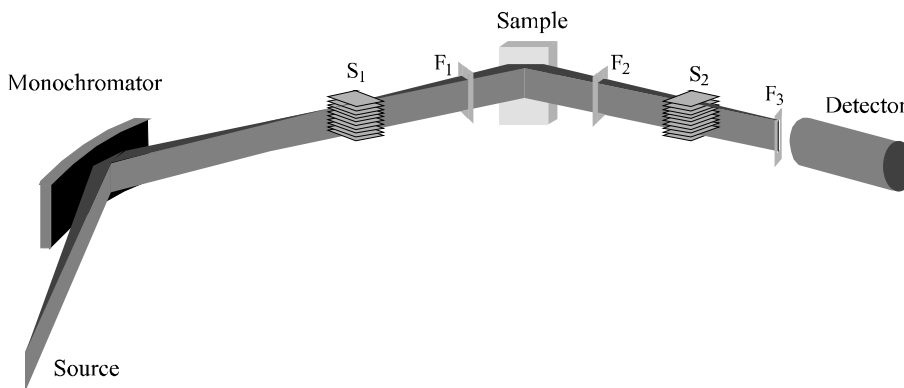

Figure 2.51. *Path of the X-ray beams in a Bragg-Brentano diffractometer equipped with a front monochromator*

Another possibility consists of placing the monochromator on the path of the beams diffracted by the sample, a configuration referred to as a back monochromator. It helps prevent parasite radiation, such as that caused by the sample's fluorescence hitting the detector.
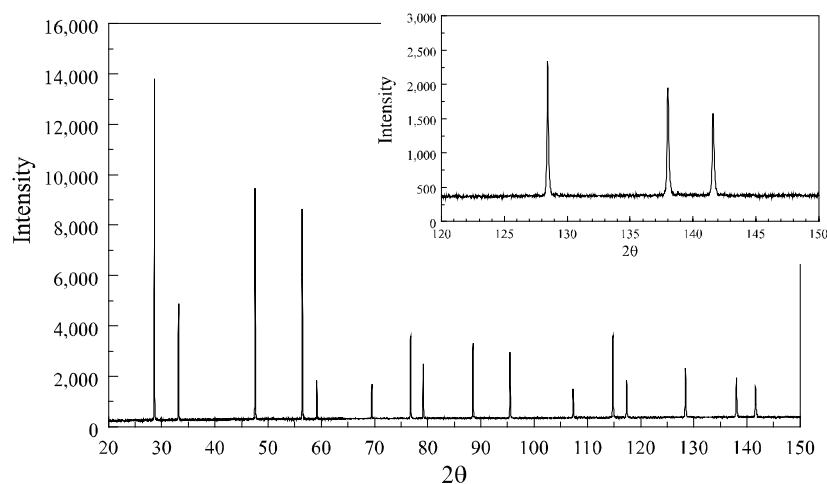

Figure 2.52. *Diffraction pattern of a sample of cerium oxide powder obtained by using a Bragg-Brentano diffractometer equipped with a copper anode and front quartz monochromator [BAL 04]*

In Brentano's original configuration, the direct beam directly irradiates the sample, as shown in Figure 2.48. We saw that these set-ups systematically produce diagrams with peaks split in two due to the presence of the $K_{\alpha 1}$-$K_{\alpha 2}$ doublet. We also mentioned that the main advantage of Bragg-Brentano diffractometers is the possibility to have a high angular resolution, because the diffracted beams are detected where they converge. The angular resolution functions of these systems are sometimes determined by only taking into account the width of the diffraction peaks' $K_{\alpha 1}$ components but, as discussed by Langford and Louër [LAN 96], this approach is not entirely correct. The presence of the component due to the $K_{\alpha 2}$ radiation causes a significant increase in the partial overlap of the peaks, which complicates the processing of the diffraction diagrams a great deal. The usual approach [RAC 48] for processing the results of diagrams comprising split peaks is to set the intensity ratio between the peak caused by the $K_{\alpha 1}$ radiation and the peak caused by the $K_{\alpha 2}$ radiation. We have already mentioned in the first part of this chapter [DEU 95, DEU 96, DIA 00] that a description of the Kα radiation's actual form is much more complex. Therefore, this approach is just an approximation, and it is particularly difficult to find a precise model to predict the shapes of the

diffraction peaks obtained with devices not equipped with a monochromator. This does not constitute an actual problem if the purpose of processing the pattern is to determine the integrated intensities, but it makes the analysis of the peak profiles very difficult. Therefore, even though the use of a monochromatic beam is always the better option [OET 99], structural studies that are led from the measurements of the integrated intensities can be conducted based on the pattern obtained using diffractometers equipped with absorption filters [LOU 88, HIL 92, HIL 94, CUS 99]. On the other hand, in the case of microstructural studies, the information sought is related to the shape of the diffraction peaks, requiring an analysis of the peak profiles, which means that in those cases, a system equipped with a front monochromator is necessary [LAN 96, SYN 99].

As we have shown, the Bragg-Brentano diffractometer imposes, by definition, the use of a punctual detector. Under these conditions, and aside from improving the efficiency of detectors, reducing the acquisition time can only be done by increasing the intensity of the incident beam, that is, either by using a high intensity source (rotating anode generator or synchrotron source), or by increasing the ratio between the intensity of the beam originating from the monochromator and that of the beam produced by the source. The increase of this ratio can be achieved by increasing the mosaicity of the monochromator crystal. Note, however, that this increase in mosaicity causes at the same time a decrease in wavelength selectivity. Thus, the use of an elliptical artificial crystal causes a significant increase in the flow of X-rays irradiating the sample, but at the same time causes a strong decrease in the device's angular resolution, since these monochromators are unable to separate the $K_{\alpha1}$-$K_{\alpha2}$ doublet.

A few authors have suggested replacing the punctual detector by a position sensitive linear detector [GOB 79]. This reduces the acquisition time, meaning that these systems can be used to study the *in situ* structural transformations associated, for example, with temperature variations. However, the diffracted beams are detected outside of their focusing points, thus greatly deteriorating the angular resolution [STO 01, CHE 04]. Most of the time, position sensitive detectors are linear gas detectors placed so that they are tangent to the goniometric circle and present an angular opening of several degrees. Generally speaking, this configuration results in a poor angular resolution, with acquisition times that remain longer than those obtained with Debye-Scherrer and Hull systems, which use curved position sensitive detectors. An interesting compromise between acquisition speed and angular resolution was recently suggested [REI 02]. This author used a real-time multiple strip, solid, position sensitive detector which makes it possible to choose an angular opening adapted to the beam's imperfections. We know that the focusing in a Bragg-Brentano system is approximate (the sample is tangent to the focusing circle and also, the size of the source is not infinitely small), which led to the idea of choosing an angular opening that generally corresponds to the actual size of the diffracted beam when it reaches the detection circle (goniometric circle). When the Bragg-Brentano diffractometer is used in low

resolution configurations, in other words, with an absorption filter and relatively open windows, the detector's entrance slits can have a size of 2°, thus reducing the acquisition time by a factor of up to 100! [REI 02]. In the high resolution mode, this opening has to be significantly reduced. Nonetheless, by choosing an opening in the range of a quarter of a degree, the resolution function's quality is not diminished, whereas the acquisition time is reduced by a factor 10.

2.2.3.3. *Depth and irradiated volume*

We will determine later on, when describing systems designed for the study of thin layers, the general expressions of the irradiated volume and of the penetration depth according to the incidence angle and the diffraction angle. However, it is rather easy to note in the case of Bragg-Brentano diffractometers, for which the incidence angle is always equal to the Bragg angle, that the irradiated volume is unaffected by variations of θ. However, as the diagram in Figure 2.53 shows, the penetration depth varies with the angle θ. These two characteristics of the acquisition conditions for patterns produced using these systems has a considerable effect on how they are used. Since the irradiated volume is constant for any diffraction angle, the intensities diffracted for the different peaks can be directly compared. On the other hand, because the depth of the analysis varies with the diffraction angle, the sample has to be perfectly homogenous with respect to its thickness. If this condition is not met, the resulting pattern is difficult to use, because the various peaks do not correspond to identical areas in the sample. In practice, this happens fairly often, particularly with bulky samples that have undergone a thermal process. This characteristic prohibits the use of these systems in cases where the sample is a layer thin enough for the X-ray beam to go through it ($\approx \mu$m).
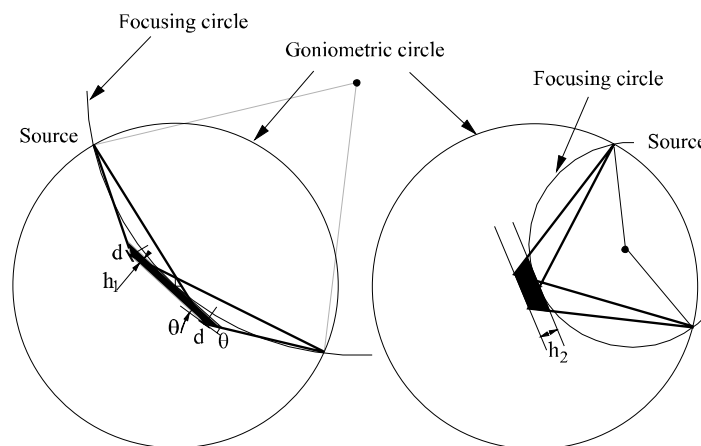

Figure 2.53. *Variations of the irradiated depth and surface with the Bragg angle*
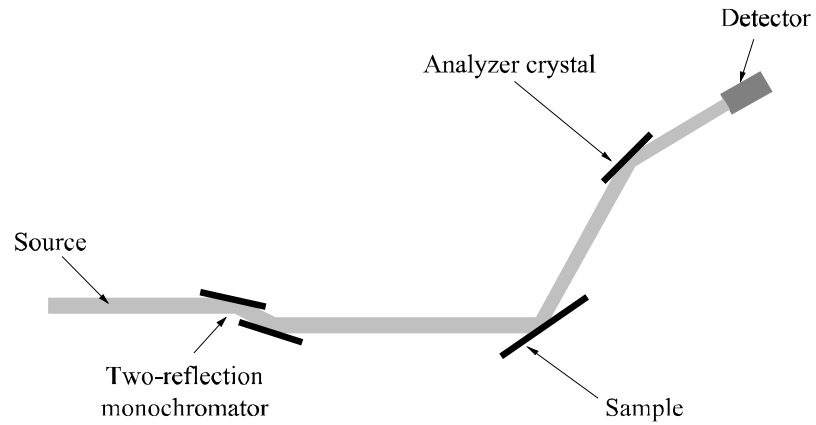
2.2.4. *Parallel geometry diffractometers*

The three types of diffractometers we have just described use divergent X-ray sources. As we have seen, this leads to the problem of detecting the beams diffracted by the sample as close as possible to where they converge. These diffractometers were designed in the first part of the 20th century, at a time when all of the available X-ray sources provided divergent beams. The advent of synchrotron radiation sources, which produce practically parallel beams, led to the design of diffractometers based on these sources, created for the study of polycrystalline samples with parallel beams [FIT 95, HAS 84]. Since the beginning of the 1990s, experimental laboratory set-ups based on this geometry have started to appear.
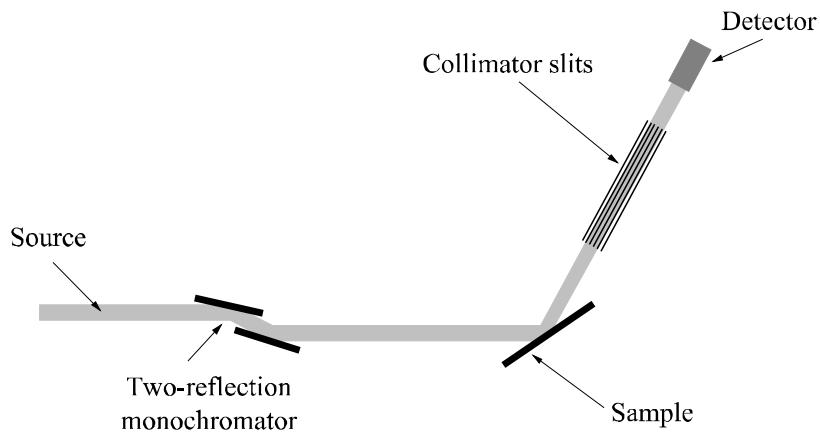
We will not describe here in detail the diffractometers installed on synchrotron sources, since they almost always consist of prototypes adapted to a particular type of study and measurement. We can point out, however, that since the source directly produces a parallel beam, the diffracted beams will be non-divergent regardless of the sample's shape (capillary, plane, transmission, reflection, etc.).

Generally speaking, in these systems, the beam originating from the storage ring is diffracted by a double crystal, often made out of silicon. This beam then irradiates the sample (plane or capillary) and the beams diffracted by the sample are again diffracted by a plane crystal[7], before being picked up by the detector (see Figure 2.54a). This analyzer crystal can be replaced with a set of slits comprised of relatively long, parallel plates. The spaces between these plates and their lengths define the angular opening and therefore the diffractometer's angular resolution (see Figure 2.54b).

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7 This crystal makes it possible to select a specific wavelength bandwidth. By analogy with spectroscopic methods, it is referred to as an analyzer crystal.

(a) Use of an analyzer crystal

(b) Use of back collimator slits

Figure 2.54. *Geometrical arrangement of diffractometers for polycrystalline samples using a synchrotron source*

Since the middle of the 1990s, some authors [SCH 96, FUG 99, GRO 98a] have suggested creating parallel geometry devices in laboratories designed by using the same idea as diffractometers installed on synchrotron sources. Naturally, the main problem in this case is the intensity of the incident beam. This is why, in most cases, the multi-reflection, front monochromator is replaced with a parabolic multi-layer

monochromator. The beam produced by the source is diffracted by the multi-layer monochromator and then by the sample. The divergence of the beam originating from this type of monochromator is typically in the range of a few hundredths of a degree[8] [JIA 02]. Usually, collimator slits are placed in the back (see Figure 2.55). This configuration makes it possible to obtain diffraction patterns with very short exposure times. The main advantage of these diffractometers is that, because of the analyzer crystal (or of the back collimator slits), the position of the sample has little influence on the measurements [SCH 96], thus making it possible to produce diffraction patterns with samples that have irregular surfaces. However, as we have already mentioned, these multi-layer monochromators cannot select the $K_{\alpha1}$ peak, resulting in split peaks. The use of an analyzer crystal instead of collimator slits can sometimes help solve this problem.
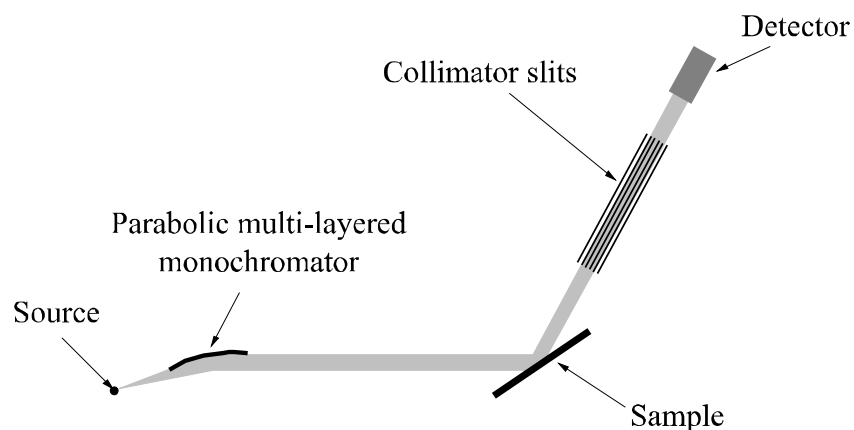

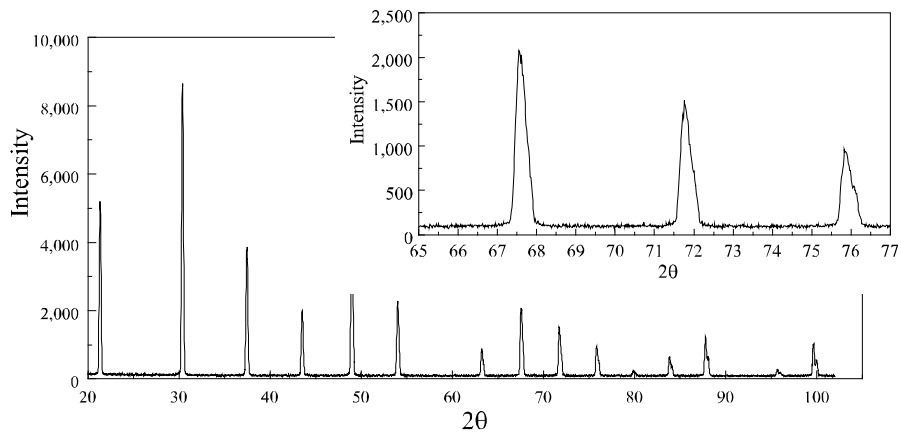**Figure 2.55.** *Parallel geometry configuration in the laboratory*

We saw that the parallel beam originating from the parabolic, multi-layered monochromator is wider than the initial X-ray focusing spot. Therefore, the resulting diffraction peaks should be wider. The device's actual resolution increases when the space between the plates comprising the collimator slits decreases. The decrease of this opening, however, will of course cause the intensity to decrease. Shown in Figure 2.56 are three diffraction patterns produced by using a standard sample of lanthanum hexaboride provided by National Institute of Standards and Technology. The first was obtained on a device equipped with a

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8 The divergence of a beam originating from a Bartels four-reflection monochromator is typically 12 arcseconds, or 2.7 thousandths of a degree. Note that, in the case of parabolic multi-layer monochromator, the divergence is 10 times that.
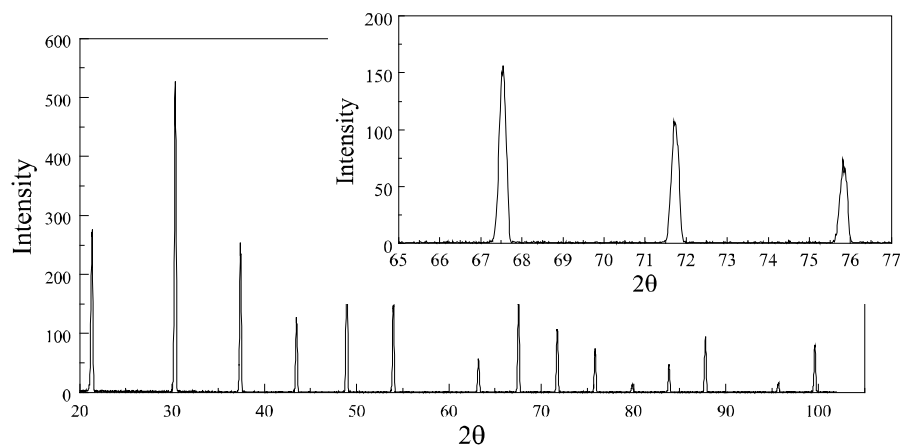
parabolic, multi-layered monochromator and collimator slits, and the second was produced with an analyzer crystal and a front hybrid monochromator, comprised of a multi-layered parabolic monochromator and two plane germanium crystals. The third, finally, was obtained with a Bragg-Brentano device equipped with a front monochromator made out of quartz.

Quite clearly, the Bragg-Brentano diffractometer leads to the best angular resolution. The peaks which are split in two, specific to the $K_{\alpha 1}$ and $K_{\alpha 2}$ emission peaks, are plainly visible in the first pattern . The peaks in the second pattern are not split, but they are clearly wider than those obtained with the Bragg-Brentano diffractometer.
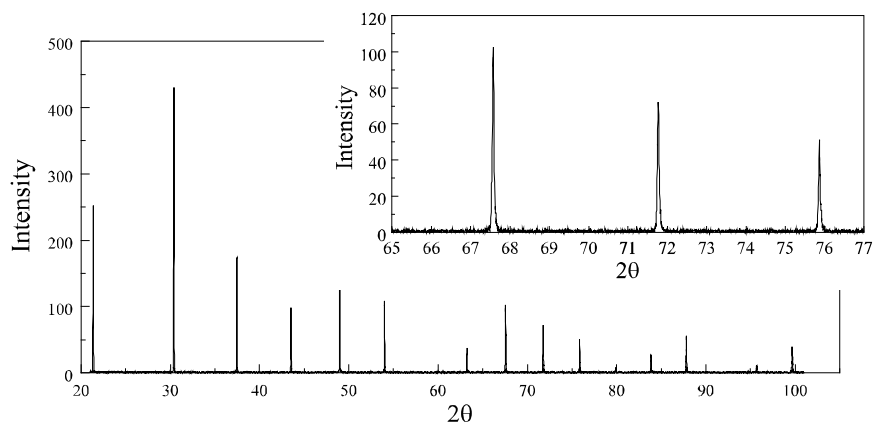
These laboratory parallel geometry configurations lead to average angular resolutions, but have the advantage of requiring limited acquisition times. Therefore, they are used for applications where the acquisition speed is a key factor. From this point of view, they constitute an alternative to the Debye-Scherrer and Hull systems with a curved position sensitive detector, for example, when conducting thermodiffraction measurements.

(a) X-ray diffraction pattern of an LaB_6 sample obtained by using a parallel geometry device with a parabolic multi-layered monochromator and collimator slits

(b) X-ray diffraction pattern of an LaB$_6$ sample obtained by using a parallel geometry device with a hybrid monochromator and an analyzer crystal

(c) X-ray diffraction pattern of an LaB$_6$ sample obtained by using a Bragg-Brentano device with a front monochromator made out of quartz

Figure 2.56. *Comparison of patterns obtained with laboratory systems working in parallel geometry or in the Bragg-Brentano configuration. These patterns were realized by Vermulen from the PANAlytical company*

2.2.5. *Diffractometers equipped with plane detectors*

It is a well-known fact that the diffraction figure of a monochromatic X-ray beam with a polycrystalline sample comprised of crystals with random orientations is a set of diffraction cones that all have the same apices. The intersection of these cones with a plane orthogonal to their axis corresponds to the Debye-Scherrer rings. In all of the diffractometers we have described in this book, the diffracted intensity is measured for a specific radius of these rings, meaning that most of this diffracted intensity is lost. In the case of samples that have a certain texture, the rings are discontinuous and this information does not appear, or appears only indirectly when the measurements are performed with the devices we have just described. The use of plane detectors can simultaneously solve these two problems, and usually leads in particular to excellent measurement statistics. Strictly speaking, traditional photographic plates are plane detectors, but the information obtained is not directly digital. It is only very recently, with the arrival of plane gas or solid detectors (CCD or imaging plate detectors), that two-dimensional diffraction measurements on polycrystalline samples have started to appear. The main problem remains the detector's size since, for a given wavelength, the device's angular resolution increases proportionally to the distance between the detector and the sample, but the detector's size quickly becomes very large. In practice, this is certainly the feature that limits the most the development of this type of device.

The first studies led with these systems used synchrotron radiation [GUA 96, NOR 97]. These authors used a plane, imaging plate detector and showed that the patterns produced by integrating the intensity along the Debye-Scherrer rings can lead to data with a quality suitable for structural analysis. One of the problems is that the distance between the sample and different points of the detector is variable; in other words, a parallax effect is observed. This effect has to be corrected digitally. A slightly different approach consists of using curved two-dimensional detectors. The optimal situation would consist of designing spherical detectors. It would seem that such detectors are not currently technologically feasible. However, other authors have suggested using cylindrical imaging plate detectors [ROB 98, TAK 98].

Recently, these studies have led to the production of laboratory diffractometers. Stachs and his collaborators [STA 00], for example, built a device equipped with a rotating anode generator and a cylindrical two-dimensional imaging plate detector. The maximum size of these detectors, currently the largest on the market, is close to 30 cm in diameter. Despite this size, the measurement of diffraction peaks corresponding to relatively small interplanar distances can only be achieved, with this type of device, if the incident beam's wavelength is small. These authors used the Kα radiation of a silver anode tube. However, this choice leads to a significant overlap of the peaks. Other authors performed the same type of measurements with

a two-dimensional gas detector [HE 02, DIC 02]. Since the size of these detectors is limited to about 10 cm, they are unable to completely measure Debye-Scherrer rings. Today, this type of device is essentially used for texture measurements. One of the big advantages of these diffraction systems with two-dimensional detection is that they do not require any movement on the part of the detector. This feature can prove to be crucial in extreme conditions. Such a diffractometer was built, for example, with a plane CCD detector in order to perform measurements on Mars [SAR 05a, SAR 05b].

These studies, which have been led since the beginning of this new century, show that it is now possible to obtain two-dimensional measurements of the intensity diffracted by a polycrystalline sample. However, several questions involving the optics and the angular resolution remain unanswered. For example, the angular resolution of such devices is directly related to the size of the beam, which usually has a square or circular cross-section and has to be as small as possible. The development of micro-sources could help to meet this condition [STA 00], but the number of crystals in the Bragg position is then quite low, resulting in poor measurement statistics. A possible solution would be to have the sample continuously oscillate during the measurement [SAR 05a]. The main problem remains the limited size of the detectors. This aspect could be gradually solved and these devices might see important developments in the years to come.

We have described in detail the features of the different types of diffractometers used for diffraction on polycrystalline samples. The analyzed samples take various forms, can be powdery or bulky, and can be analyzed in transmission or in reflection. Virtually all existing diffractometers can be described based one or the other of these typical configurations. We should point out, however, that samples in the form of thin films are a different matter and diffractometers designed for the study of these samples have to be adapted. We will detail in the following sections the characteristics of these diffraction systems.

2.3. Diffractometers designed for the study of thin films

2.3.1. *Fundamental problem*

2.3.1.1. *Introduction*

The energy of the X-ray beams used in radiocrystallography, while rather high, is small enough for the penetration depth of this radiation to be no greater than a few micrometers. If the devices used are adapted accordingly, X-ray diffraction should then make it possible to characterize thin films. For about 20 years, researchers in