This lecture is part of the Basic XRD Course.
A perfect polycrystalline sample should contain a large number of crystallites. Ideally, we should always be able to find a set of crystallites with a particular crystallographic direction for every orientation. In that case, the sample is considered ‘randomly oriented’.
Various degrees of crystallites orientation distribution can be found in a sample. On one extreme, a single crystal has its crystallographic direction pointing only in one direction. On the other side, a randomly oriented powder or polycrystalline sample has all orientations possible for a particular crystallographic direction. In between, there are samples that have a preferred orientation, meaning that some specific crystallographic direction can only be found at particular orientation in the sample. This is often the case with highly anisotropic crystallites like clays mineral, in which the crystallites are found with their (001) planes parallel to the surface.
The two main parameters in a symmetric XRD scan are $\theta$, the angle between the incident beam and the sample surface, and $2\theta$, the angle made by the incident and diffracted beam.
The gonio scan is normally used for both qualitative and quantitative phase analysis of powder samples. In such a measurement, both $2\theta$ and $\theta$ vary while keeping their mutual relation $\theta = 2\theta/2$. That means that $\omega = \theta$ and that the angle between the incident beam and the sample is equal to the angle between the sample and the diffracted beam. Due to this symmetry, the gonio scan is also called symmetric scan.

It is important to point out that during all the measurements, only crystallites having planes parallel to the surface can participate to the diffracted signal.
In a gonio scan, only the planes parallel to the surface are observed. Other crystallites still diffract but the detector is not in the right position to observe these other signals. As $\theta$ and $2\theta$ move, the diffracted signal of different plane families is collected.
An X-ray diffraction (XRD) scan is a collection of X-ray intensities as we vary a defined parameter. In most XRD scans, we change $2\theta$ and $\theta$ at the same time ($\theta$ being scanned at half the speed of $2\theta$). In a gonio scan, the data (X-ray intensity) are plotted against $2\theta$ scale (x-axis). Peaks can be observed when diffraction occurs for a specific set of planes and when the detector is positioned at the right angle to collect the diffracted signal.

A gonio scan is performed: let’s look to the first part. Below 20 °$2\theta$, no diffracted signal is observed. On the scheme, the incidence angle of the beam is set at the right angle so that the blue crystallite satisfies the Bragg law. However, the diffracted beam is not observed by the detector, since its position is set to observe crystallites with lattice planes parallel to the surface.
The gonio scan continues. At $2\theta = 21.5^\circ$ ($\theta = 10.75^\circ$), crystallites with their (001) planes parallel to the surface satisfy the Bragg law condition. Since the detector is now at the right angle, the diffracted signal of the (001) planes parallel to the surface is measured.

The properties of the diffraction peak, like its full width at half maximum (FWHM) and its intensity, will also be influenced by the optics used at the incident and diffracted beam side. This will be discussed in the coming lectures.
The gonio scan continues. At $2\theta = 30.5^\circ$, crystallites with their (011) planes parallel to the surface satisfy the Bragg law. These planes have a smaller interplanar distance, so the diffracted angle is higher.
The gonio scan is finished. We can observe the diffracted signal of the different planes of the CsCl structure. Only crystallites with their planes parallel to the surface have been observed. The crystallites that have contributed to the diffraction of the (001) planes are not the same that contributed to produce the diffraction signal of the (011) planes. However, the crystallites that have participated to the diffracted signal of the (002) planes are the same crystallites as the ones contributing to the (001) diffracted signal, since these sets of planes are parallel to each other.
Para-focusing geometry means that the divergent beam irradiating the sample is re-focused on the detector at the same distance from the sample as the one between the incident beam and the sample.

This is possible thanks to the random orientation of the crystallites in the sample. As shown in the slide, the center of the beam (full line), which determines the $\theta$ angle, is diffracted right on the detector for a particular set of planes $(h_1,k_1,l_1)$. Due to the divergence of the beam, some X-rays irradiate the sample at an incident angle slightly higher (long dashed line) or lower (dashed line) than $\theta$. These X-rays will irradiate also crystallites with their $(h_1,k_1,l_1)$ planes oriented in such a way that diffraction occurs. The resulting diffracted beam will be focused on the detector.

By increasing the divergence of the beam, the area irradiated is increased, as well as the number of crystallites orientations that can contribute to the diffracted signal.

In this kind of geometry, the peak positions are sensitive to the sample height. Therefore, the height of the sample must be aligned very carefully prior to the measurements.
This type of scan is similar to the gonio scan, but with an offset on the incident angle value. In a gonio scan, this offset is equal to zero. Offset values are generally a few degrees only for phase analysis and larger for stress measurements.
When measuring a thin film over a single crystal, keep in mind that some peaks of the substrate, which have high intensity, can cover peaks of the top layers. To avoid the diffraction of the single crystal, an offset is applied so that the substrate planes do not satisfy the diffraction condition. On the contrary, the top layers crystallites diffract, assuming that they are randomly oriented.
The main application for 2θ scans is measurement of thin films. The angle of incidence is usually low (below 10°). Those kind of measurements are often called grazing incidence scans.
X-rays have a specific penetration depth characteristic of each material. Usually, this depth is about 10 to 100 micrometers. For thin film with a thickness of few micrometers or less, this means that the main contribution to the diffracted signal comes from the substrate.

By using a grazing incidence angle, the path of the X-rays in the sample is kept constant and is mainly going through the thin film instead of the substrate. Since the path length is a function of the incident angle, the irradiated area can be considerably longer than in a normal gonio scan. Therefore, the irradiated volume of the thin film is increased, as well as the chances that the X-rays interact with the thin film material. The diffracted signal, measured for the thin film, is expected to be higher than for a normal gonio scan.
In this slide, we compare two scans of a Diamond thin film grown on top of a Mo₂C substrate. The main interest of the measurement is the diamond layer. By performing a gonio scan, most of the volume irradiated is within the Mo₂C substrate, while, by choosing a grazing incidence angle, the volume in the top layer is enhanced and therefore its diffracted measured intensity is increased.
The $\omega$ scan is rarely used for powder applications. Powders samples with highly preferred orientation might require such a scan to find the optimal $\omega$ offset for a particular $2\theta$ position.

The $\omega$ scan is often used for single crystals to find the offset of the substrate plane with respect to the sample surface. This particular case is beyond the scope of this course.
Depending on the type of diffractometer, the ω scan will be done by moving different parts. For a θ-θ goniometer, both the X-ray source and the detector arm will move, keeping the value 2θ as a fixed value. For a 2θ-θ goniometer, only the sample is moved (or ‘rocked’) while the incident beam and detector positions are kept fixed. This is why this kind of measurement is often called ‘Rocking curve’.
This is an example of an ω scan on a bulk Si crystal, with its (111) plane normal orientated perpendicular to the surface. The 2θ value was kept fixed at the theoretical diffraction angle of the Si (111) planes, while the sample was moved along the ω axis. The high intensity of the peak is due to the high number of atomic planes participating to the diffracted signal.

When performing the same type of scan on a pressed Si powder, the resulting peak is much broader. This reflects the multiple orientations of the crystallites within the sample.
Summary

- Different crystallites are observed depending of the type of scan used
- Each type of scan has its specific application