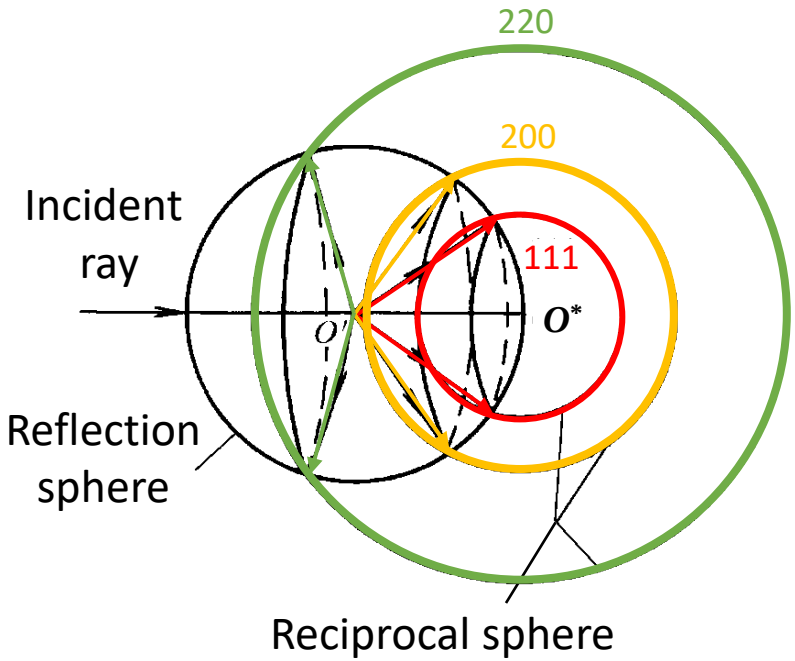
# 4. Polycrystal analysis methods

# Contents

## **4.1** Debye-Scherrer method

In polycrystals, the grain orientations are chaotically distributed, and the reciprocal lattice points with different reciprocal vector lengths (crystal planes with different inter-plane spacing) will respectively fall into the sphere with the reciprocal origin O* as the center of the sphere and the reciprocal vector length as the radius. On a series of concentric spheres, these balls are called reciprocal spheres.

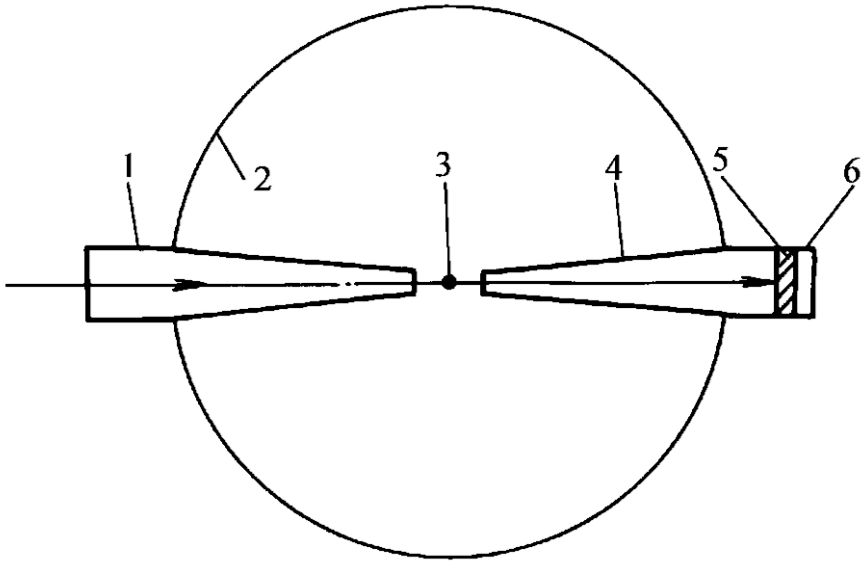



All crystal planes corresponding to the reciprocal points that intersect the reflection sphere can produce reflections. The intersection line between the reflection sphere and each reciprocal sphere is a circle, and the diffraction rays constitute a number of diffraction lines with O' as the vertex and the incident ray as the axis. The Debye pattern is a series of concentric diffraction rings or a series of diffraction arc segments.

## **4.1** Debye-Scherrer method

- Camera, film installation and specimens

X-rays enter from the center of the aperture, irradiate the cylindrical sample, and then enter the light tube.



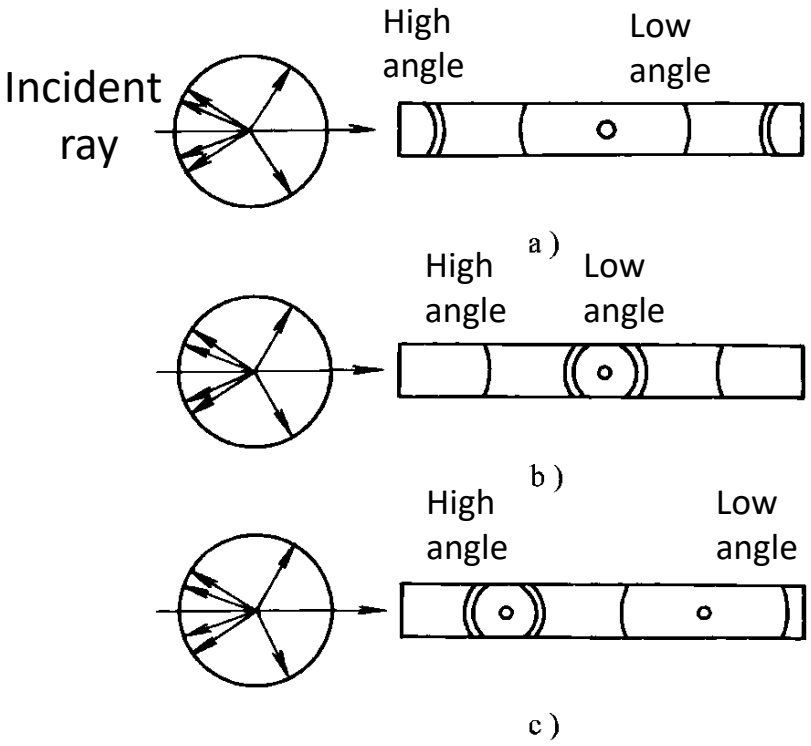

**1**. Diaphragm **2**. Shell **3**. Sample **4**. Light tube **5**. Fluorescent screen **6**. Lead glass

The camera is a cylindrical cassette with a diameter generally 57.3 mm or 114.6 mm; the sample is about 10 mm long and 0.2~1.0 mm in diameter. During the exposure process, the sample rotates around the camera axis to increase the number of diffraction grains involved.

## **4.1** Debye-Scherrer method

- Camera, film installation and specimens

The film is enclosed in the inner cavity of the camera housing, and there are three installation methods:




1. X-rays are injected from the film interface and emitted from the central hole. The geometric relationship and calculation are simple and used for general phase analysis.

2. X-rays are injected from the center hole of the film and emitted from the interface. The spectral lines are recorded, and the shrinkage error of the film is small. It is suitable for measuring lattice parameters.

3. X-rays enter and exit from the two holes in the film, which can directly calculate the camera perimeter and eliminate errors such as film shrinkage. It is a commonly used method.

## **4.1** Debye-Scherrer method

- Selection of photographic protocols

1. The general principle of X-ray tube anode target is $Z_{target} \leq Z_{sample}$; if this cannot be satisfied, the selection limit is $Z_{target} = Z_{sample} + 1$; for samples with extremely small $Z$, select Cu or Mo target.
2. Filter piece When $Z_{target}$ is smaller than 40, $Z_{filter} = Z_{target} - 1$; When $Z_{target}$ is larger than 40, $Z_{filter} = Z_{target} - 2$.
3. Tube voltage: The tube voltage is 3 to 5 times the critical excitation voltage of the anode target ***K*** family.
4. Tube current: Tube current cannot exceed the maximum allowable tube current.
5. Exposure time is usually determined through experiments because the exposure time is related to many factors such as the choice of specimen, camera, and the photography procedures. If a Cu target and a small-diameter camera are used to photograph a Cu sample, the exposure time is 30 minutes. If a Co target is used to photograph an Fe sample, it will take 2 hours.

## **4.1** Debye-Scherrer method

- Selection of photographic protocols

Commonly used data for photographing powder phases

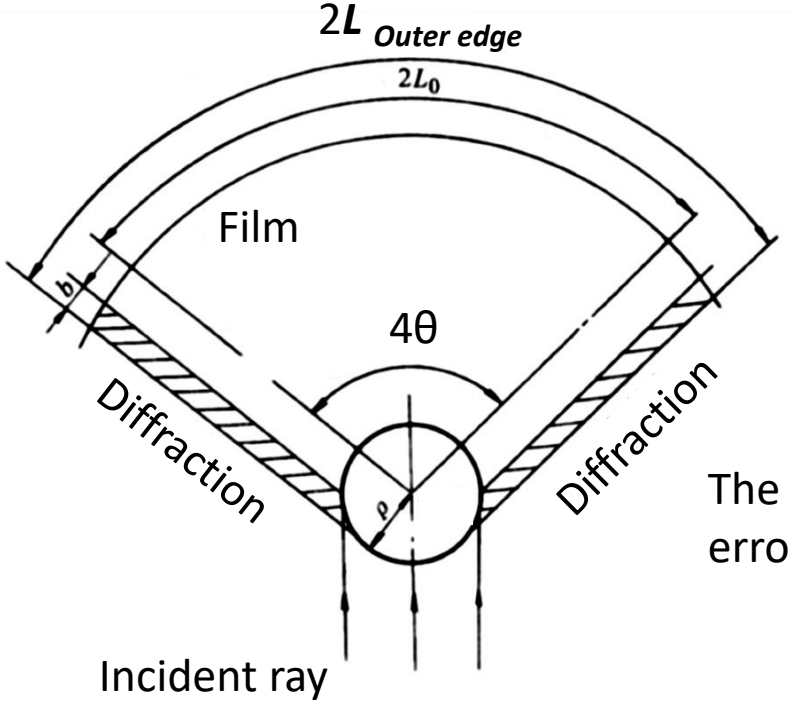
| Target (anode) | Cr | Fe | Co | Ni | Cu | Mo |
|---|---|---|---|---|---|---|
| $U_K$, kV | 5.98 | 7.10 | 7.71 | 8.29 | 8.86 | 20.0 |
| $U$, kV | 20~25 | 25~30 | 30 | 30~35 | 35~40 | 50~55 |
| Filter | V | Mn | Fe | Co | Ni | Zr |
| $\lambda_{K\alpha1}$, nm | 0.228970 | 0.193604 | 0.178897 | 0.165791 | 0.154056 | 0.070930 |
| $\lambda_{K\alpha2}$, nm | 0.229361 | 0.193998 | 0.179285 | 0.166175 | 0.154440 | 0.071359 |
| $\lambda_{K\alpha}$, nm | 0.229100 | 0.193736 | 0.179026 | 0.165919 | 0.154184 | 0.071073 |
| $\lambda_{K\beta}$, nm | 0.208487 | 0.175661 | 0.162079 | 0.150014 | 0.139222 | 0.063229 |
| $\lambda_K$, nm | 0.207020 | 0.174346 | 0.160815 | 0.148807 | 0.138059 | 0.061978 |

# **4.1** Debye-Scherrer method

- Errors and corrections

1. Sample absorption error

The absorption of X-rays by the sample will cause the diffraction lines to deviate from the theoretical position. X-rays irradiate a sample with a radius of $\rho$, producing a diffraction cone with a vertex angle of $4\theta$, and the average theoretical distance between diffraction arc pairs on the film is $2L_0$. However, due to the absorption of the sample, the arc pair spacing of the diffraction lines increases, and the diffraction lines have a certain width $b$.




The distance between the arc and the outer edge is $2L_{Out\ edge}$, then we have

$$2L_0 = 2L_{Outer\ edge} - 2\rho$$

The above formula can be used to correct the position error of diffraction lines caused by sample absorption.

## **4.1** Debye-Scherrer method

- Errors and corrections

2. Film expansion and shrinkage error

From Figure 1, the glancing angle θ = (2L / 2πR) X 90° can be calculated using 2L. However, due to camera accuracy, film installation, film expansion and shrinkage, etc., there are errors in the calculation of the θ angle.

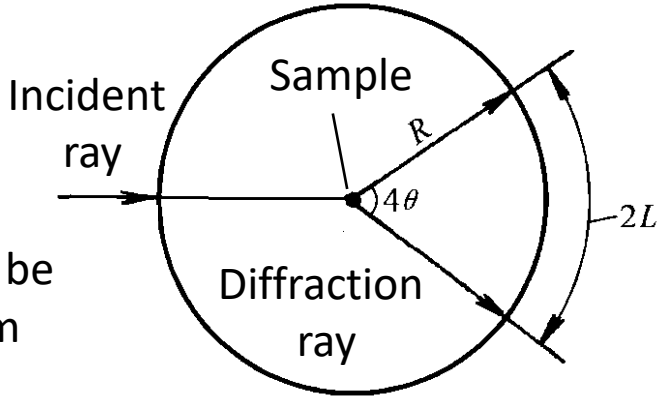
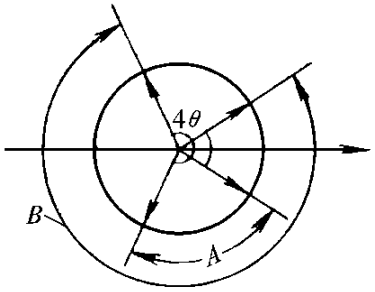



Figure 1



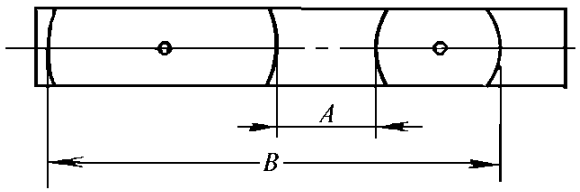




Figure 2

The measurement of the effective perimeter $C_0$ of the film is shown in Figure 2, and it can be obtained:

$$C_0 = A + B$$

Use $2L_0$ and $C_0$ to get a more accurate value of θ

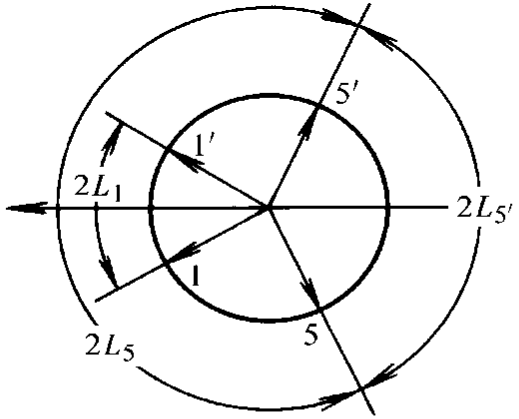
$$\theta = \frac{90^\circ}{C_0} \cdot 2L_0 = K \cdot 2L_0$$

The K value is constant for a certain film.

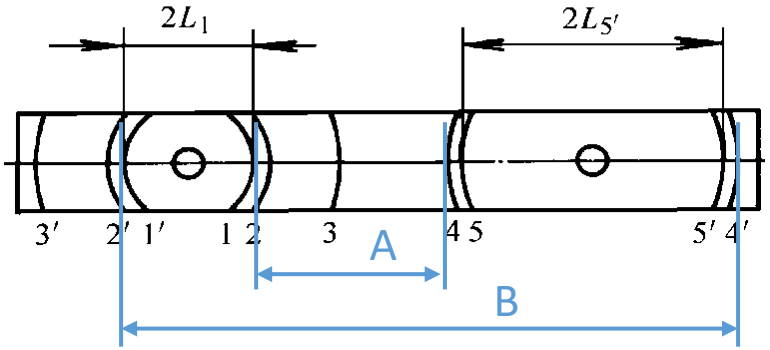
## **4.1** Debye-Scherrer method

- Calculation of the Debye phase of cubic lattice system

Before measurement and calculation, it is necessary to determine the film installation method and distinguish between high-angle areas and low-angle areas. The calculation steps are as follows:




Low angle




1. Mark the numbers of the arc, starting from low angle area to high angle area **1–1'**, **2-2'**, **3-3'**…..

2. Measure $C_0$. Select an arc pair in the high and low angle areas, measure A and B, and use formula (page 9) to calculate $C_0$.

$$C_0 = A + B$$

3. Measure and calculate the arc pair spacing $L_0$. Measure the arc pair spacing $2L_1$, $2L_2$, $2L_3$, etc. The low-angle area can be measured directly. For the arc pair in the high-angle area, such as 5-5', can be measured instead as $2L_{5'}$, $2L_5 = C_0 - 2L_{5'}$, and the equation (page 8) is used to correct and calculate $2L_0$.

$$2L_0 = 2L_{Outer\ edge} - 2\rho$$

## **4.1** Debye-Scherrer method

- Calculation of the Debye phase of cubic lattice system

4. Calculate θ: Use equation (page 9) to calculate the θ value series corresponding to the $2L_0$ series.

Step 3

$$\theta = \frac{90^\circ}{C_0} \cdot 2L_0 = K \cdot 2L_0$$

Step 2

$\theta_1\ \theta_2\ \theta_3\ \theta_4\ \theta_5$ .....

5. Calculate ***d*** Use Bragg's equation to calculate the ***d*** corresponding to the θ value. If the $K_\alpha$ double lines in the high-angle area can be separated, $\lambda$ takes the corresponding value; otherwise, the weighted average of the double lines is taken.

$$d = \frac{\lambda}{2\sin\theta}$$

$d_1, d_2, d_3, d_4, d_5$ ...

6. Estimate the relative intensity of each diffraction line $I/I_1$: $I_1$ refers to the intensity of the strongest line, and $I$ is the intensity of any line. Visual inspection sets the strongest line strength as 100 (i.e., 100%), and the rest can be set as 90, 80, 50, etc.

$I_1, I_2, I_3, I_4, I_5$ ...

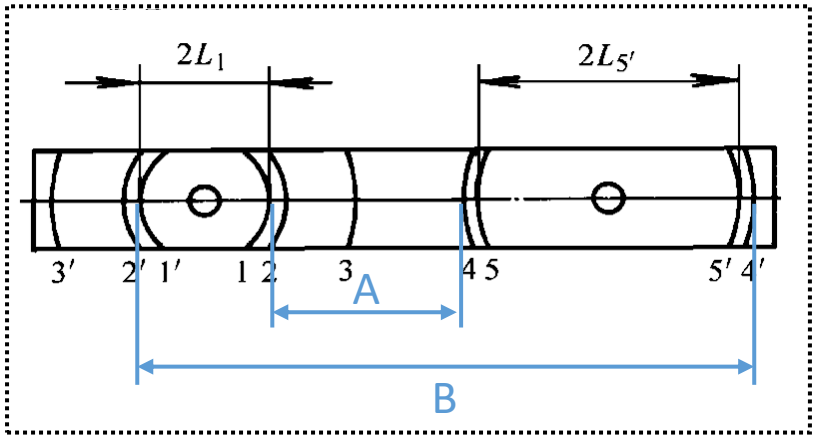
7. Check card: According to ***d*** series and ***I*** series, compare the material standard card. If both series agree well with the card, the phase of the object can be determined. Among them, the ***d*** series is the main basis for physical phase identification.

## **4.1** Debye-Scherrer method

- Calculation of the Debye phase of cubic lattice system

8. Mark the diffraction line index. Mark the corresponding diffraction line according to the crystal plane family index ***H K L*** corresponding to the d series in the card.

9. Calculate ***a***: from the cubic crystal plane spacing formula: $a = d\sqrt{H^2 + K^2 + L^2}$




$d = \dfrac{\lambda}{2\sin\theta}$ → ***I*** → Card → ***H K L*** → $a = d\sqrt{H^2 + K^2 + L^2}$

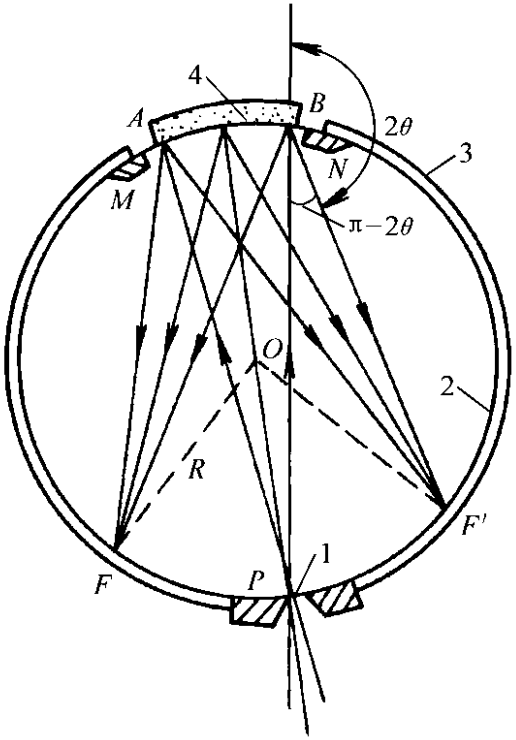
$\theta = \dfrac{90°}{C_0} \cdot 2L_0 = K \cdot 2L_0$

$C_0 = A + B$ → $2L_0 = 2L_{\text{Outer edge}} - 2\rho$

## **4.2** Other methods

- Symmetrical focus photography

This method requires that the light source, sample surface and focus point are on the same focus circle, and this circle is the camera inner wall. The specimens are made by grinding polycrystalline blocks. When divergent X-rays irradiate the sample (AB arc), the reflected ray must be focused at point F or F’ .



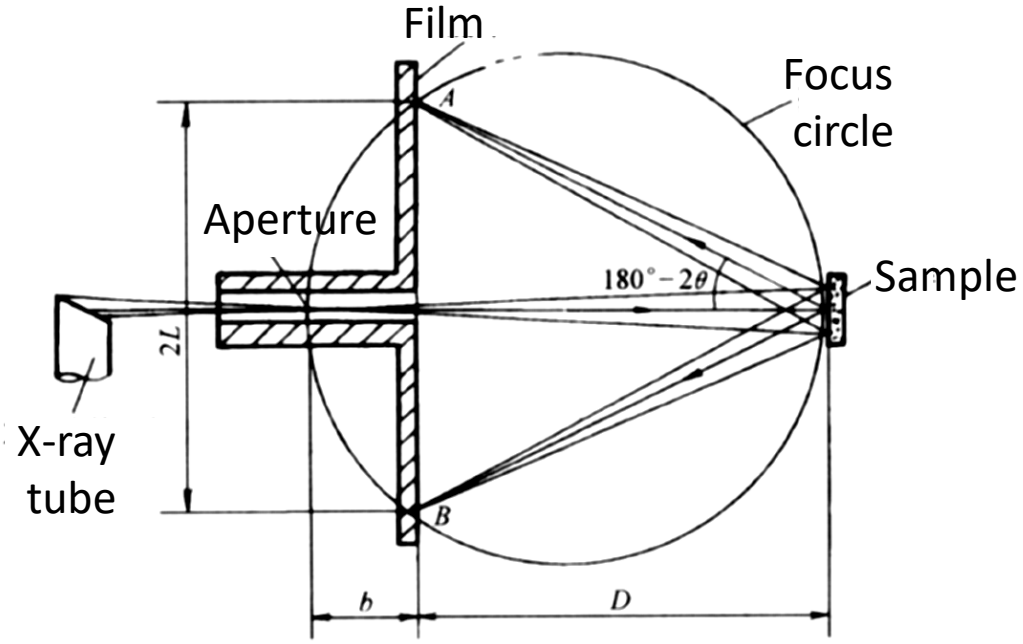

The symmetrical focusing method is conducive to capturing high-angle reflection lines, has short exposure time, and has high resolution, so it is often used for accurate determination of lattice parameters.

1 - aperture 2 - camera wall 3 - film 4 - sample

## **4.2** Other methods

- Back-illuminated plate photography (pinhole method)

The flat plate photography method is divided into two types: transmission and back-reflection. Figure is a schematic diagram of the back-reflection flat plate photography method. Because the diameter of the focusing circle is large, flat specimens are generally used. This method requires that the four points A and B of the sample, aperture and diffraction ring are co-circular, and the sample is tangent to the circle.




Its diffraction pattern consists of concentric diffraction rings. Because there are too few diffraction rings, it is not suitable for phase analysis. It is used to study grain size, preferred orientation, crystal integrity, and accurate determination of lattice parameters.

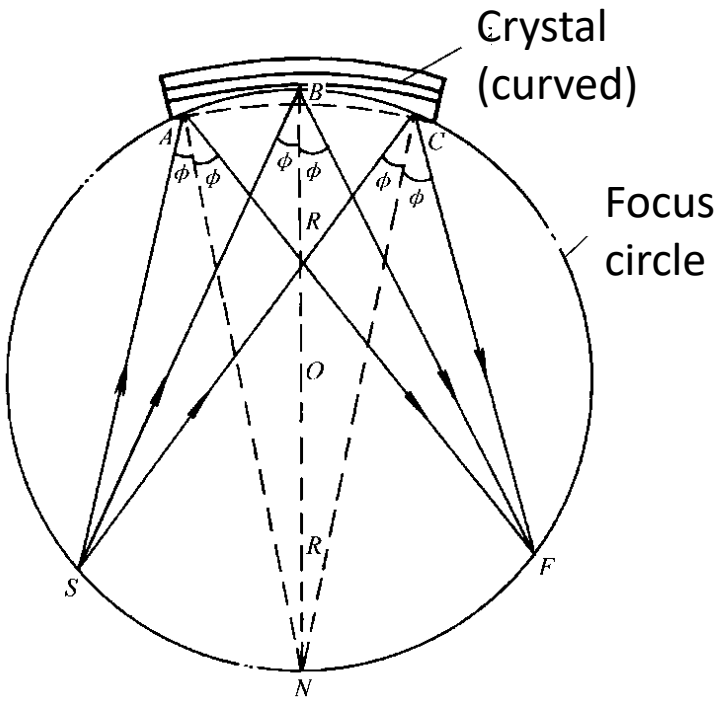
$$L = D\tan(\pi - 2\theta)$$

$$b = D\tan^2(\pi - 2\theta)$$

## **4.2** Other methods

- Crystal monochromator

Make a crystal plane with strong reflective ability of a single crystal parallel to the outer surface, adjust the direction of the incident ray to meet the Bragg condition, and reflect strong monochromatic light. The reflection efficiency of bent monochromatic crystals is higher. The principle is shown in the figure. The X-rays emitted from the light source S are illuminated at each point of the curved monochromatic crystal ABC, and the reflected lines will converge to the focus F.




At present, X-ray diffractometers have commonly used graphite bent crystal monochromators, which have high reflection efficiency and can obtain diffraction patterns with extremely low background.

## **4.3** X-ray diffractometer

- Before the 1950s, X-ray diffraction analysis basically used films to record diffraction patterns, that is, various photographic techniques.
- Now, X-ray diffractometer has basically replaced photography and is widely used in many research fields.
- Diffractometer measurement has the advantages of convenience, speed, and accuracy. It is combined with a computer to largely automate its operation, data measurement, and processing.
- X-ray diffractometer mainly consists of X-ray generator, goniometer, radiation detector, recording unit and automatic control unit, among which the goniometer is the core component of the instrument.

# **4.3** X-ray diffractometer

- Overview

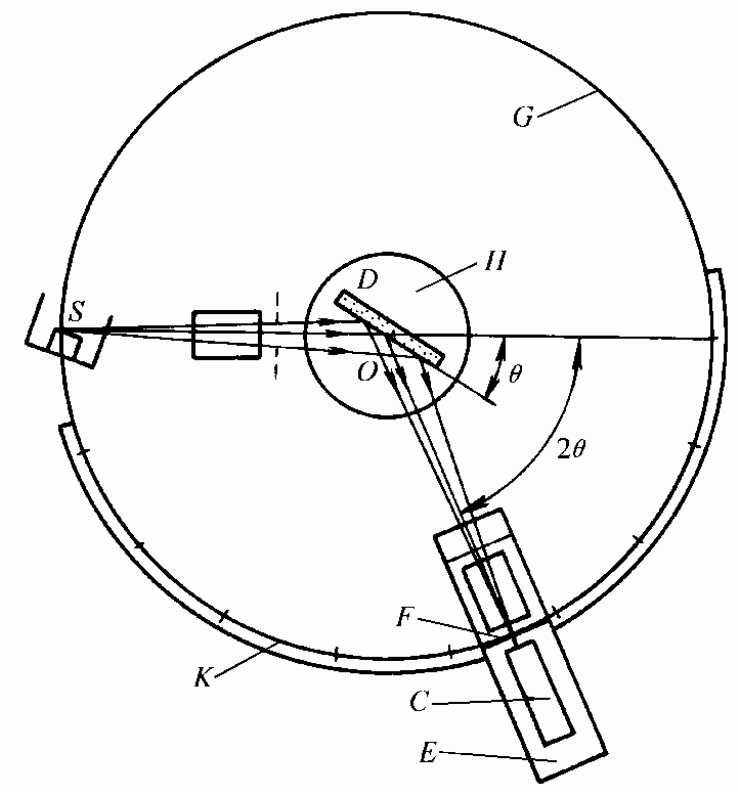


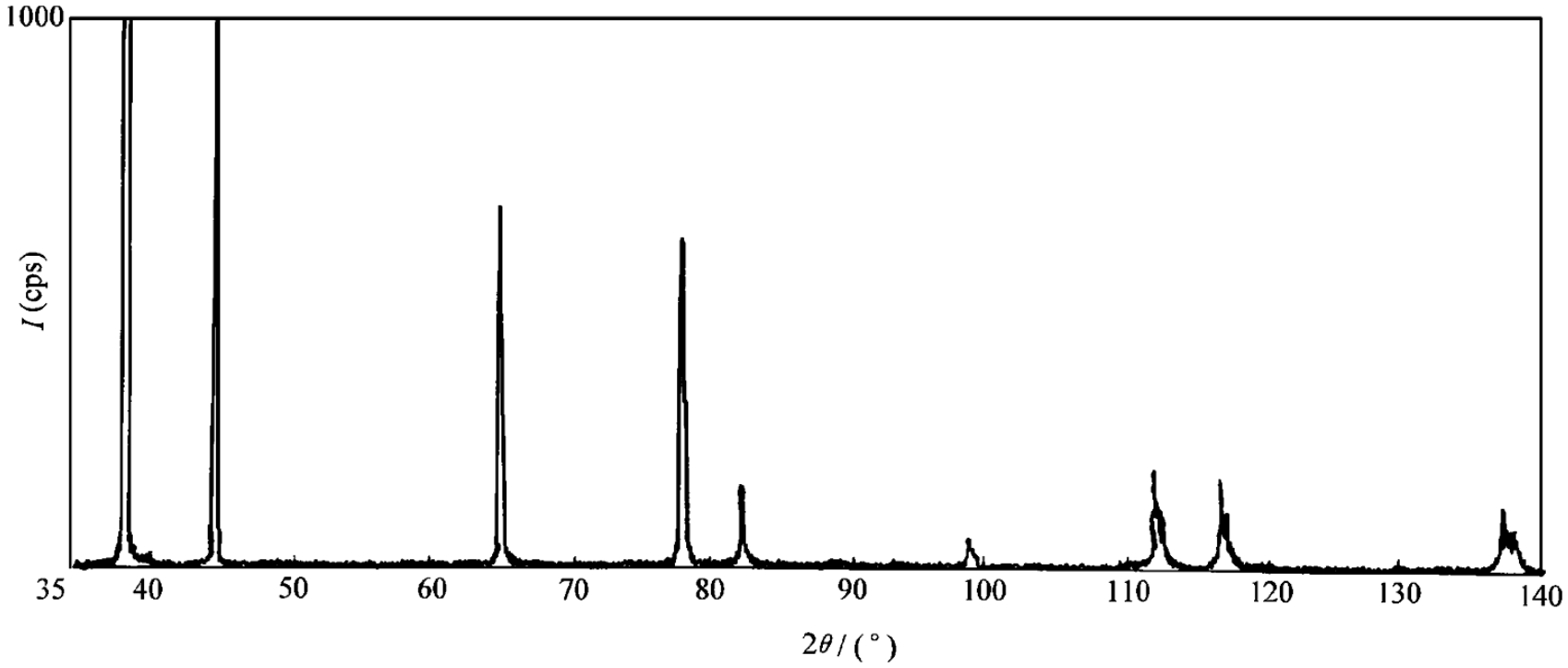

Figure is a schematic diagram of a goniometer. The flat sample D is installed on the sample stage H that can rotate around the axis O. When a beam of divergent X-rays emitted from S hits the sample, the crystal plane that satisfies the Bragg condition , its reflection line forms a convergent beam, and the counter tube C together with the slit F rotates around O with the bracket E and receives the reflection line at an appropriate position. The goniometer maintains the linkage between the sample and the counting tube, that is, the sample rotates through θ and the counting tube constantly rotates through 2θ.

G - goniometer circle, S - X-ray source, D – sample, H - sample stage, F - accepting slit, C - counting tube, E – bracket, K - scale

## **4.3** X-ray diffractometer

- Overview

When the sample and counting tube rotate continuously, the diffractometer will automatically draw a curve of the diffraction intensity changing with 2θ (called a diffraction diagram), as shown in the figure.



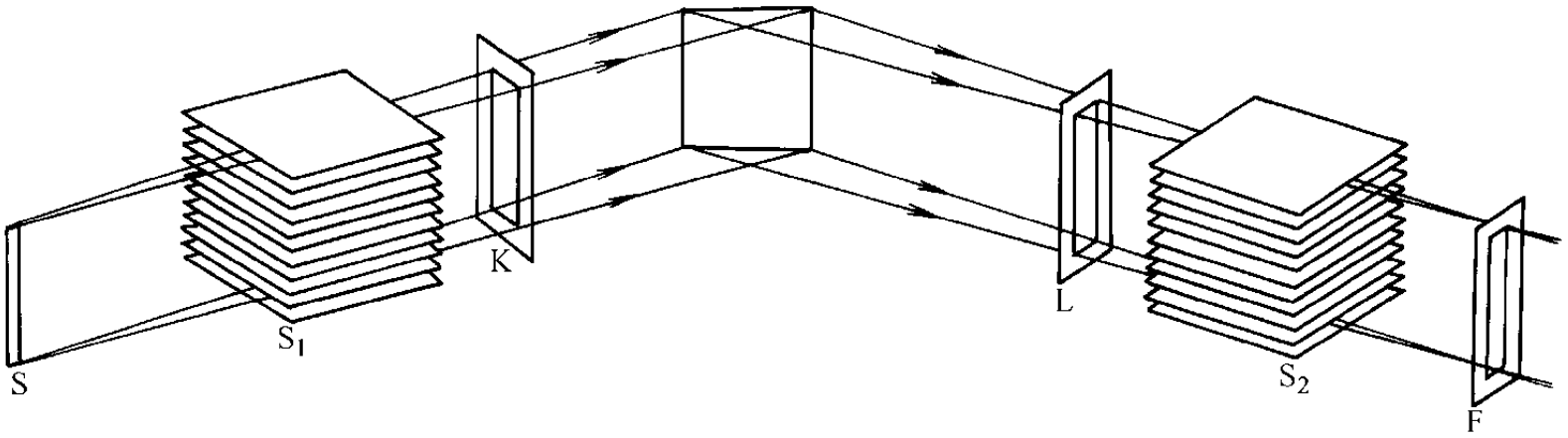
## **4.3** X-ray diffractometer

- Sample

The powder sample is pressed in the sample frame, and its particle size is about microns to tens of microns. If it is too coarse, the diffraction intensity will be unstable, and if it is too fine, the diffraction line will be broadened. Block samples can also be used, and the irradiated surface needs to be ground and etched.

- Optical arrangement

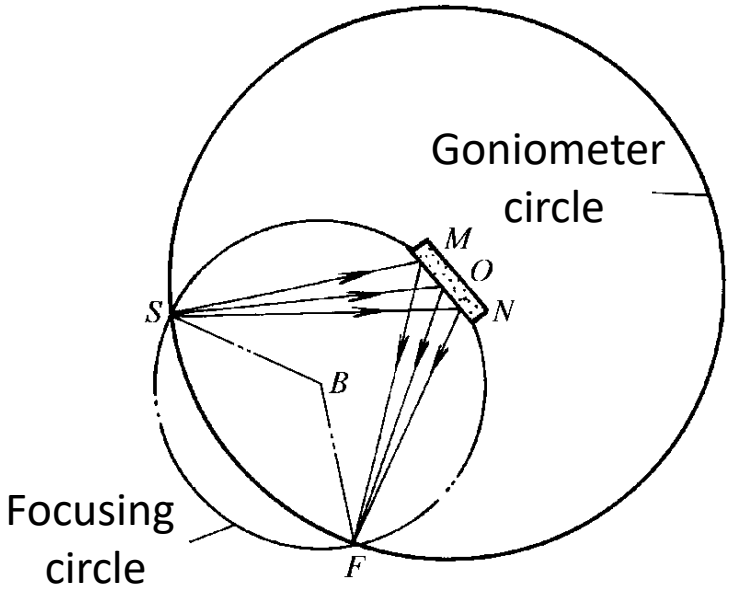
As shown in the figure, S is the line focus; K is the divergence slit, L is the anti-scattering slit, and F is the receiving slit, which limits the horizontal divergence of the ray. $S_1$ and $S_2$ are Sora slits, used to limit the divergence of rays in the vertical direction.



## **4.3** X-ray diffractometer

- Diffraction geometry

The relative position of the divergent incident ray and the flat sample causes the diffracted rays to converge exactly on the goniometer circle. As shown in Figure, in order for well-focused X-rays to enter the counting tube, it is required that the focal spot S of the X-ray tube, the irradiated surface of the sample MON, and the diffraction line convergence point F must be located on the same focusing circle.

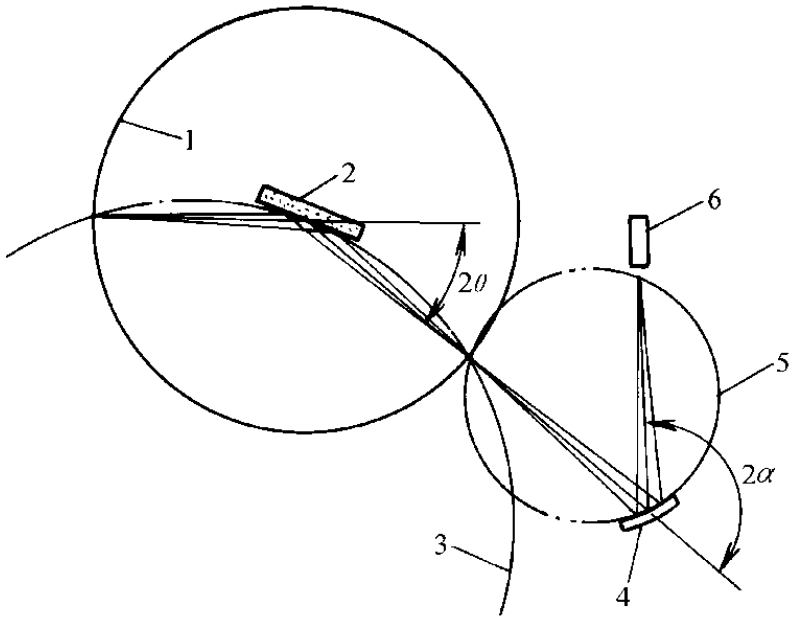



The diameter of the focusing circle changes with $\theta$. When $\theta$ is smaller, the diameter is larger. During operation, the sample and detector maintain $\theta$-2$\theta$ relation. Among the large number of crystal grains irradiated by X-rays, there are only crystal planes parallel to the sample surface (***H KL***) diffraction can occur.

## **4.3** X-ray diffractometer

- Bent crystal monochromator

The combination of a goniometer and a crystal monochromator can better eliminate $K_\beta$ rays and reduce the background caused by continuous X-rays and fluorescence radiation. Graphite bent crystal monochromators with strong reflection capabilities are now commonly used.




The diffraction rays generated by the sample are incident on the curved crystal. Adjusting the single crystal to the appropriate orientation can produce secondary diffraction. The diffraction rays enter the counting tube.

When using a monochromator, the polarization factor should be changed to $(1 + \cos^2 2\theta \cos^2 2\alpha)/2$, where $2\alpha$ is the diffraction angle of the monochromatic crystal.

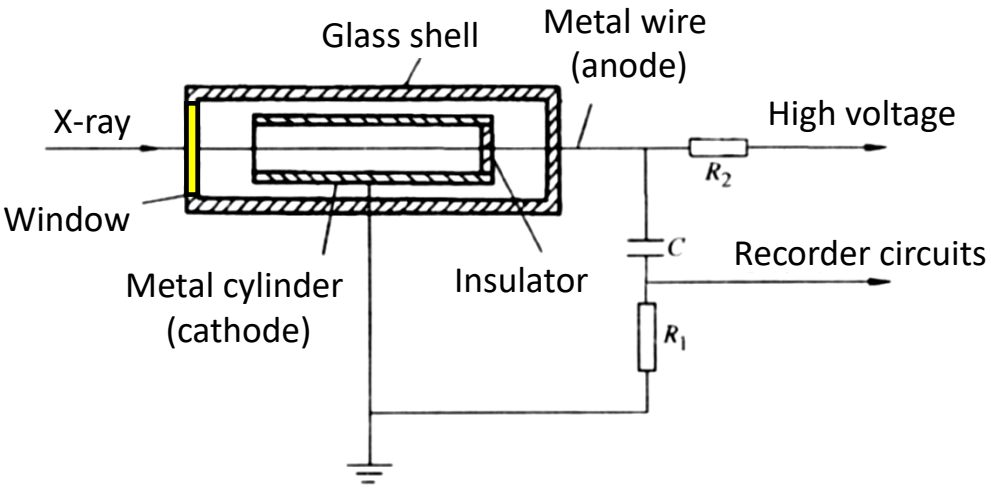
1 - Goniometer circle, 2 – Sample, 3 - Primary focusing circle, 4 - Monochromatic crystal, 5 - Second focusing circle, 6 - Counting tube

# **4.3** X-ray diffractometer

- Detection and recording system

Detector

Proportional counter (PC): As shown in Figure, a voltage (600~900V) is applied between the metal cylinder cathode and the wire anode, the glass shell is filled with inert gas, and the window is made of low absorption coefficient materials such as mica or beryllium.



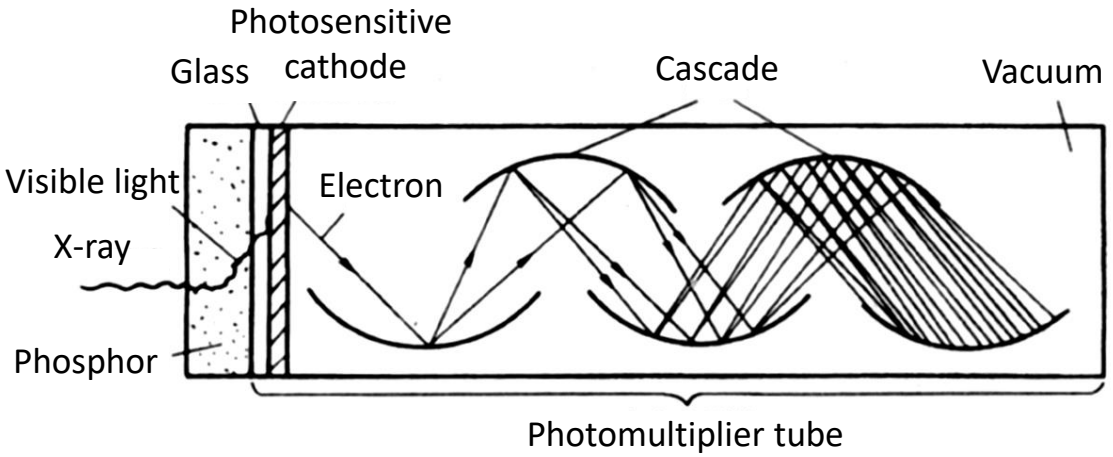

The pulse peak value output by the proportional counter is proportional to the absorbed photon energy. The intensity measurement is more reliable. It has fast response, high energy resolution, low background pulse, high counting rate and stable performance. However, it is sensitive to temperature and requires high voltage stability.

## **4.3** X-ray diffractometer

- Detection and recording system

Scintillation Counter (SC): A scintillation counter is mainly composed of phosphor and photomultiplier tube. The phosphor is generally a sodium iodide single crystal activated by adding about 0.5% thallium; the photomultiplier tube has a photosensitive cathode and 10 junctions, each junction increases the positive voltage by 100 V, and the last junction is connected to the measurement circuit.

When a crystal absorbs an X-ray, it collects a large number of electrons at the output, creating a voltage pulse.



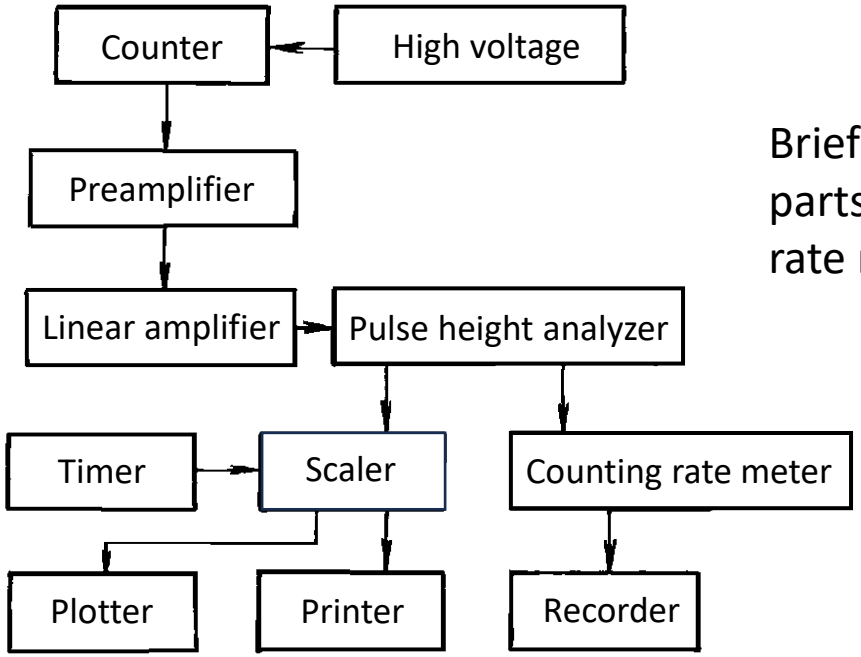

The advantage is that the resolution time is short, and the counting efficiency is high; the disadvantage is that the background pulse (thermal noise) is high, and the crystal is prone to moisture and failure.

## **4.3** X-ray diffractometer

- Detection and recording system

Main circuit for counting measurement

The main function of the counter is to convert the energy of X-rays into electrical pulse signals, and then convert the output electrical pulse signals into data that the operator can directly read or record. The counting and measurement circuit block diagram is shown in the figure.




Brief introduce the working principles of its main parts - pulse height analyzer, scaler and counting rate meter.

## **4.3** X-ray diffractometer

- Detection and recording system

Main circuit for counting measurement

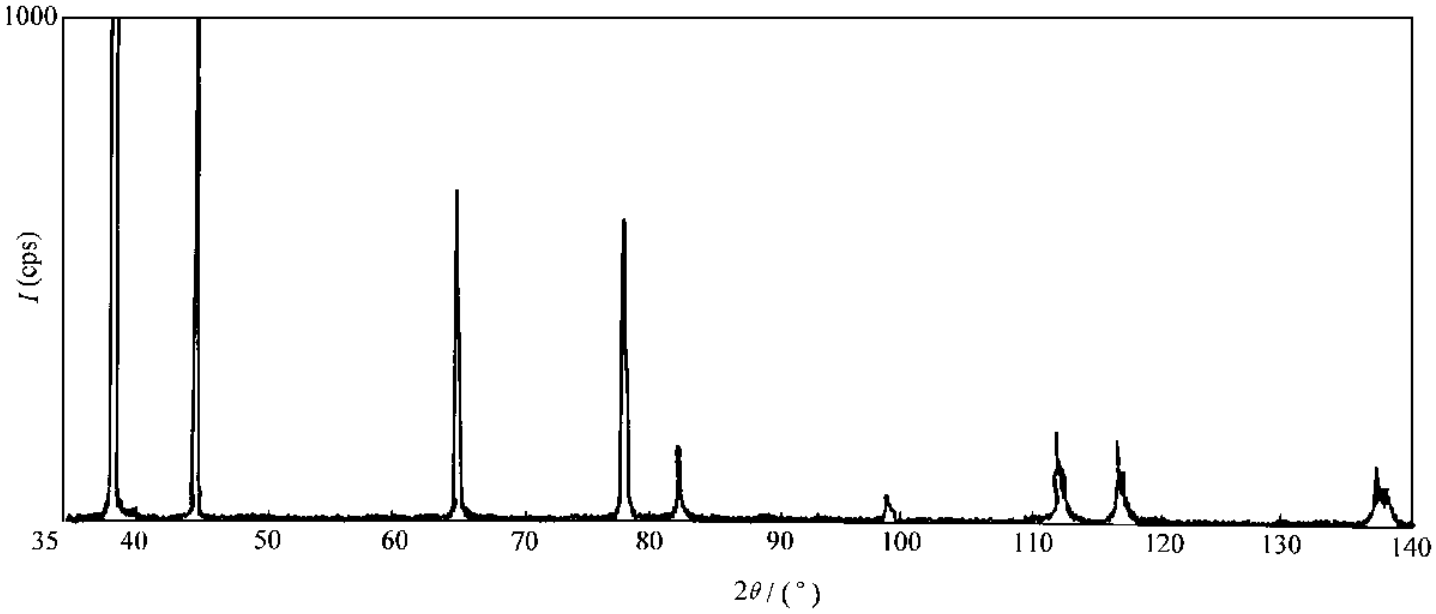
- The pulse height analyzer consists of a linear amplifier, a lower limit screening circuit, an upper limit screening circuit and an anti-coincidence circuit. Used to eliminate unnecessary interference pulses for diffraction analysis, thereby reducing background and improving peak-to-back ratio.
- Scaler: A scaler is a circuit that responds to an input pulse within a set time period. There are two methods: timing counting and fixed number counting. The larger the total number of measurement pulses, the smaller the measurement error. Therefore, it is more reasonable to use fixed number counting when comparing relative intensities. However, in order to save analysis time and facilitate use, timing counting is more preferred.
- The counting rate meter consists of a pulse shaping circuit, an RC integrating circuit and a voltage measurement circuit. Its function is to convert the input pulse signal into a DC voltage output, and then the recorder will produce a curve (diffraction pattern) of the intensity changing with the diffraction angle. The time constant must be set reasonably, otherwise the shape of the diffraction peak will be distorted, and the peak position will lag.

## **4.3** X-ray diffractometer

- Routine measurements with X-ray diffractometer

Measurement of diffraction intensity

The continuous scanning counter is connected to the counting rate meter. The goniometer is linked with $\theta$-$2\theta$, selects the appropriate angular speed, scans from the lower $2\theta$ to the required angle, and obtains a realistic diffraction picture at a faster speed. Figure, the results are shown in the figure below. The measurement accuracy of continuous scanning is affected by the scanning speed and time constant. This method is often used for qualitative phase analysis or full spectrum measurement.

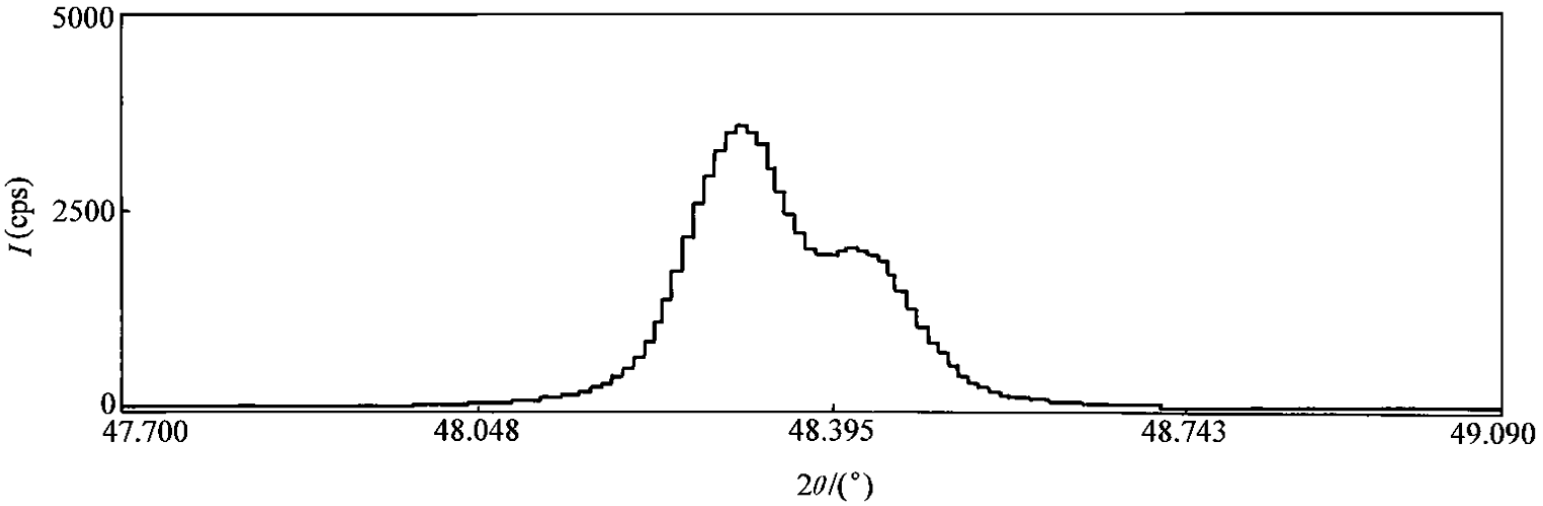


## **4.3** X-ray diffractometer

- Routine measurements with X-ray diffractometer

Measurement of diffraction intensity

The step scan counter is connected to the scaler. According to the set step width and step time, the diffraction intensity corresponding to each $2\theta$ angle is measured. The measurement results are shown in the figure. The step scan does not use a counting rate meter and has no hysteresis effect. The measurement accuracy is high. The step width and step time are important parameters that determine the measurement accuracy. This method is used to measure the intensity and position of the diffraction peak with a small angular range of $2\theta$ and to obtain the data required for linear analysis.



## **4.3** X-ray diffractometer

- Routine measurements with X-ray diffractometer

Diffraction intensity formula

The diffractometer uses a flat sample. When **θ** is small, the surface area of the sample is larger, but the effective depth of X-ray penetration is smaller. When **θ** is larger, the irradiated surface area is smaller, but the penetration depth is larger. Therefore, the irradiation volume is generally kept constant, which means that the absorption factor has nothing to do with **θ**, and the absorption factor is $1/2\mu_l$. Therefore, the single-phase polycrystalline ***H K L*** diffraction line intensity is:

$$I = I_0 \frac{\lambda^3}{32\pi R}\left(\frac{e^2}{mc^2}\right)^2 \frac{V}{V_0^{\,2}} P\left|F_{HKL}\right|^2 \frac{1+\cos^2 2\theta}{\sin^2\theta\cos\theta}\ \frac{e^{-2M}}{2\mu_l}$$

## **4.3** X-ray diffractometer

- Routine measurements with X-ray diffractometer

Selection of experimental parameters

Slit Width: Increasing the slit width can increase the diffraction intensity but results in a decrease in resolution. When analyzing the physical phase, select the divergence slit ***K*** and the anti-scattering slit ***L*** 0.5° or 1°; the receiving slit F has a significant impact on the peak intensity, peak-to-back ratio, and especially the resolution. When the diffraction intensity is sufficient, select For smaller slits, 0.2 mm or 0.4 mm is often used.

Scanning speed: Increasing the scanning speed can save test time, but it will lead to a decrease in intensity and resolution, a shift of the diffraction peak (towards the scanning direction) and asymmetric broadening. Commonly used scanning speed is 3° ~ 4°/min

Time constant: The problems caused by increasing the time constant are similar to increasing the scanning speed; however, if the time constant is too small, the background fluctuation will be intensified, making it difficult to identify weak peaks. The time constant usually selected for phase analysis is 1 ~ 4 s.