

**X-RAY DIFFRACTION (XRD)**  
and  
**XRAY POWDER DIFFRACTION (XRPD)**

Structure Determination by use of X-Rays

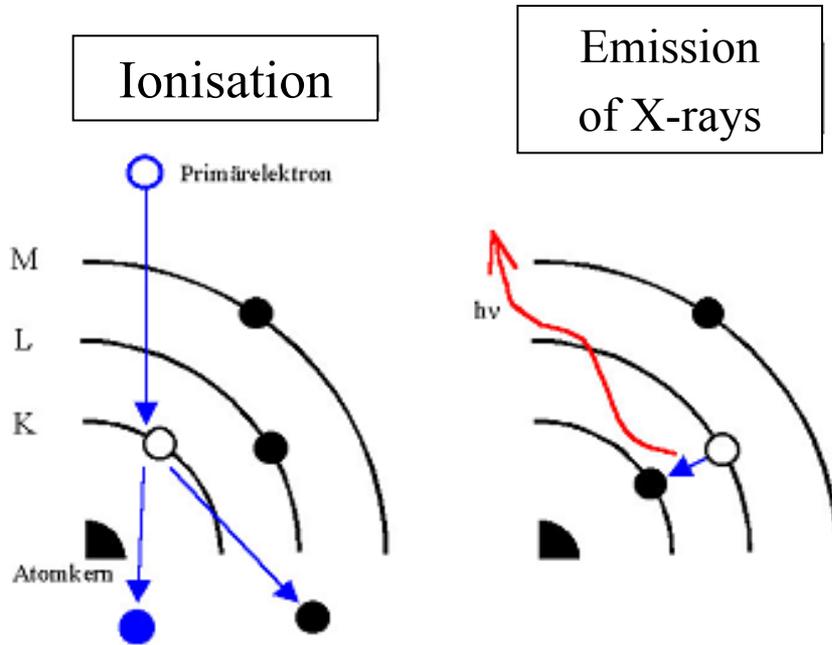
Determination of sites/positions of atoms

Crystal or X-Ray Structure Determination

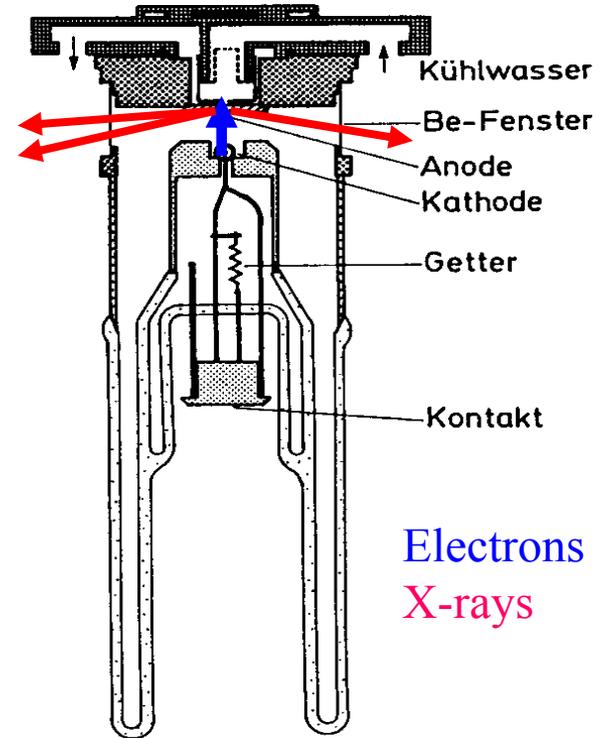
Finger print, Identification of Substances

Phase Analysis, Phase Transition Investigation

# Production of X-rays by X-ray tubes

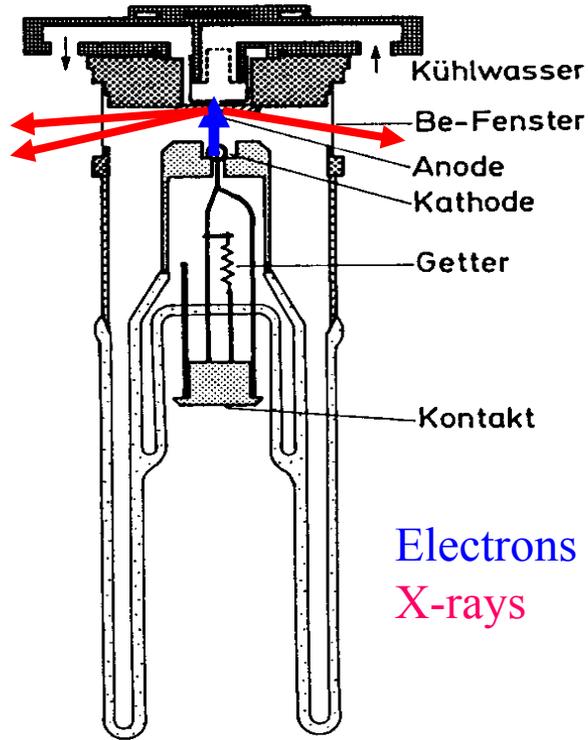


Ionisation by fast electrons  
→ Emission of X-rays



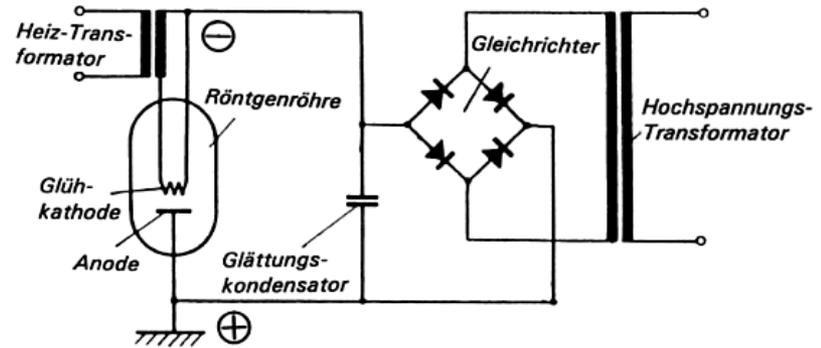
X-ray tube  
Anode (e.g. Cr, Cu, Mo)

# Production of X-rays by X-ray tubes

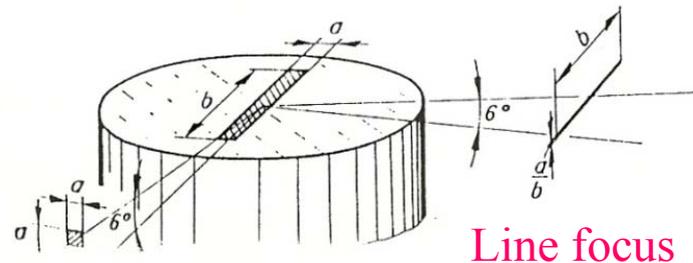


X-ray tube

Anode of e.g. Cr, Cu, Mo)



: Schaltschema eines Röntgengenerators (nach Jost, 1975).

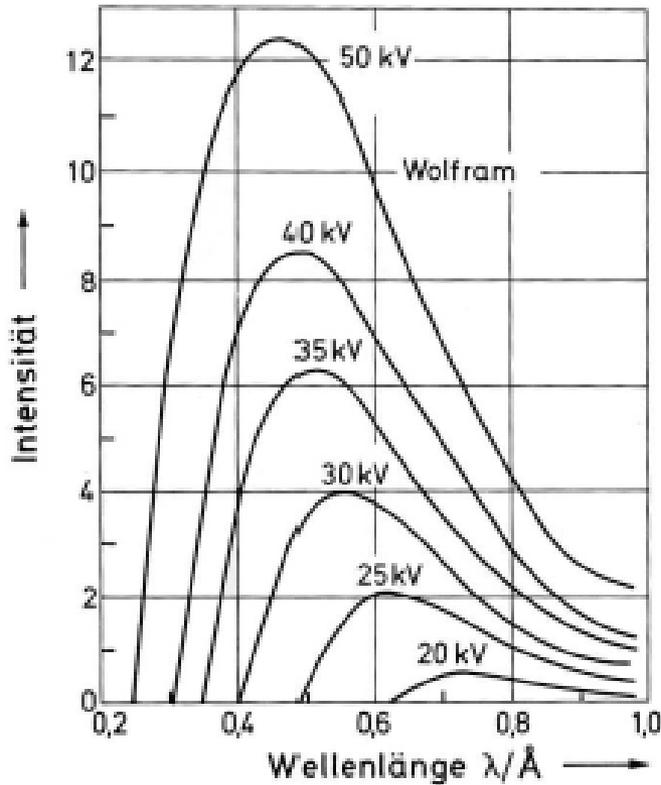


Point focus

X-ray tube

Scheme, Anode, Focus

# White/Slow and Emission Spectra of X-rays

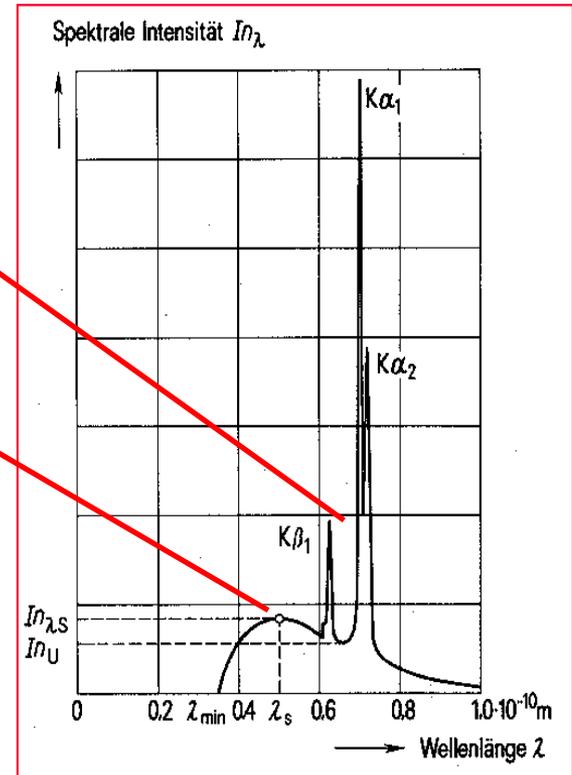


White spectra (W)

$$\lambda_{\text{Min}} [\text{\AA}] = 12.4/V [\text{kV}], \lambda_{\text{Max}} \approx 1.5 \cdot \lambda_{\text{Min}}$$

Characteristic radiation (Line spectrum)

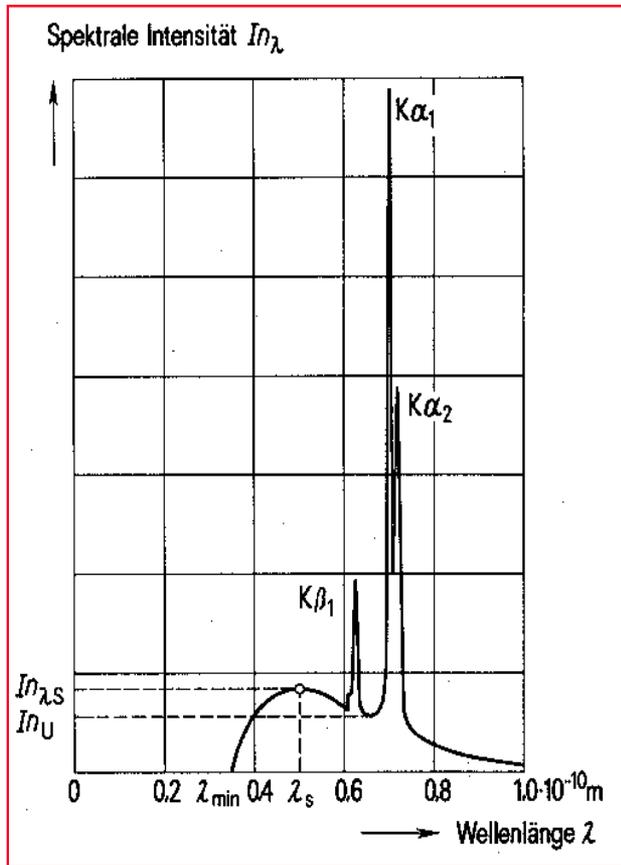
Slow radiation (Continuous spectrum)



White and emission spectra (Mo)

$$\nu_{K\alpha} \sim Z^2 \text{ (Henry Moseley, 1913)}$$

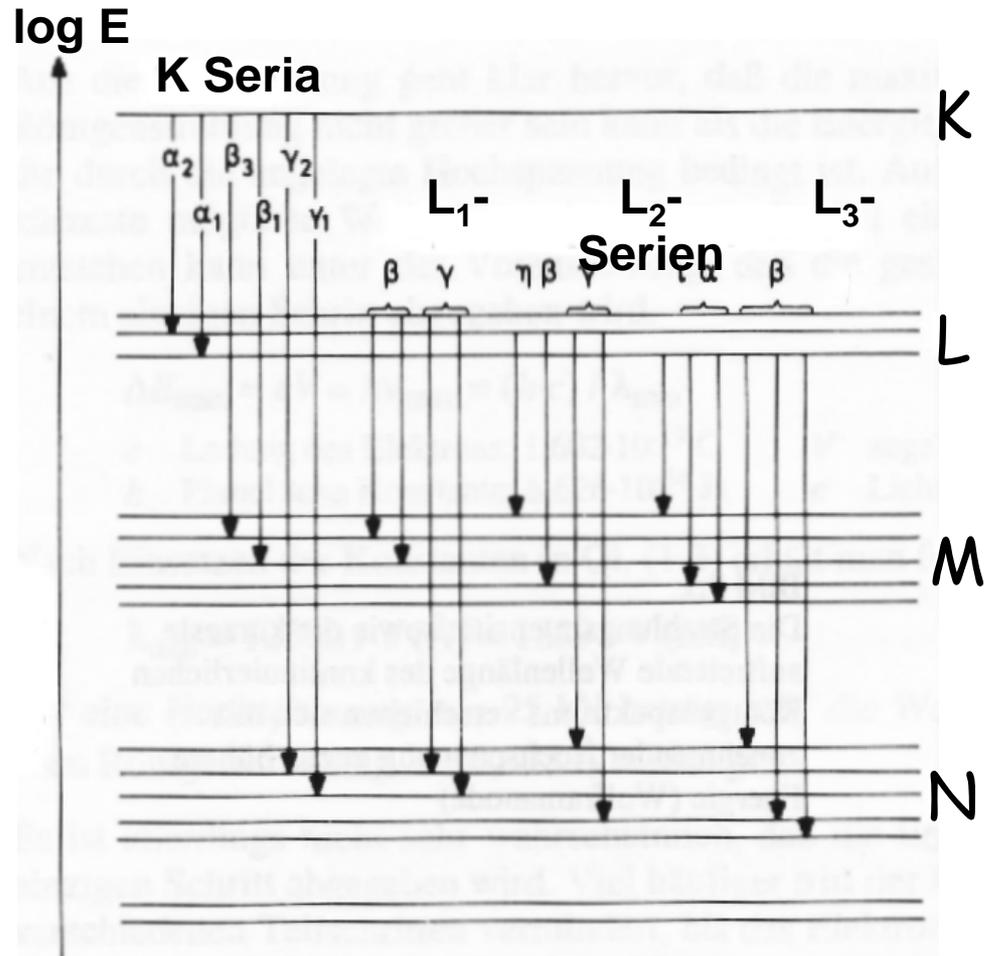
# Emission Spectrum of a X-ray Tube



Slow and emission spectra

$$\nu_{K\alpha} \sim Z^2 \text{ (Henry Moseley, 1913)}$$

$$\lambda_{\text{Min}} [\text{\AA}] = 12.4/V [\text{kV}], \lambda_{\text{Max}} \approx 1.5 \cdot \lambda_{\text{Min}}$$



Term scheme ([Auswahlregeln](#):  $2n-1$  states,  
 $1 \leq n \leq 7$ ,  $0 \leq l \leq n-1$ ,  $\Delta l = \pm 1$ ,  $-1 \leq m_l \leq +1$ ,  $\Delta m_l = 0, \pm 1$ )

# Wavelengths of different X-ray tubes

Wavelengths of the most important K series in Å \*

Atom Nr.	Element	K $\alpha$	K $\alpha_1$	K $\alpha_2$	K $\beta$
24	Chrom	2,29092	2,28962	2,29351	2,08480
26	Eisen	1,93728	1,93597	1,93991	1,75653
27	Kobalt	1,79021	1,78892	1,79278	1,62075
28	Nickel	1,65912	1,65784	1,66169	1,50010
29	Kupfer	1,54178	1,54051	1,54433	1,39217
42	Molybdän	0,71069	0,70926	0,71354	0,63225
47	Silber	0,56083	0,55936	0,56378	0,49701
74	Wolfram	0,21060	0,20899	0,21381	0,18436

\* 1 Å = 10<sup>-10</sup> m. In former times wavelengths were given in X units:

1000 X = 1KX = 1,00202 Å = 100,202 pm.

# Radiation Protection and Units for Use of X-Ray's

Activity:	Becquerel (Bq)	1 Bq = 1/s	before Curie (Ci): 1 Ci = $3,7 \times 10^{10}$ Bq
Ion dosis	(C/kg):		before Röntgen (R): 1 R = $2,6 \times 10^{-4}$ C/kg )
Energy dosis:	Gray (Gy)	1 Gy = 1 J/kg	before Rad (rd): 1 rd = 0,01 Gy
Equivalent dosis:	Sievert (Sv)	1 Sv = 1 J/kg	before Rem (rem): 1 rem = 0,01 Sv

- Activity: 1 Ci is the decay rate of 1 g  $^{226}\text{Ra}$  (historically to the honor of Marie Curie).
- Ion dosis: physically, referred to the building of ions in air.
- Energy dosis: absorbed radiation energy per mass unit.
- Equivalent dosis: measure for destruction ability of a radiaton (impact factor · energy dosis).  
Impact factor: 1 for X-rays, up to 20 for  $\alpha$ -rays.
- Natural radiation exposure:  $\sim 2,5$  mSv/a (cosmisc  $\sim 1$  mSv, terrestric  $\sim 1$  mSv, other  $\sim 0,5$  mSv),  $^{40}\text{K}$  corporated in a human body gives e.g.  $\sim 4500$  Bq ( $\sim 0,18$  mSv/a).
- Medical radiation exposure:  $\sim 1,5$  mSv/a (e.g. stomach-bowel investigations  $\sim 160$  mSv).
- Other radiation exposures (technique, atomic bombes, nuclear reactors etc.):  $\sim 0.01$ - $0.03$  mSv/a.
- 20 mSv have been fixed to be the maximum body dosis per year for exposed persons.
- 400 mSv per year are considered to be just not harmful. From 2-10 Sv serious health damages appeare. Doses of 10-15 Sv are lethal by 90-100 %, doses  $>50$  Sv are lethal by 100 % within 1h to 2 days.

→ **Use of ionizing radiation needs attention and shielding**

Literature: Hans Kiefer, Winfried Koelzer: Strahlen und Strahlenschutz, Springer-Verlag

Internet: [www.bfs.de](http://www.bfs.de) (Bundesamt für Strahlenschutz)

# Radiation Protection Needs Shielding

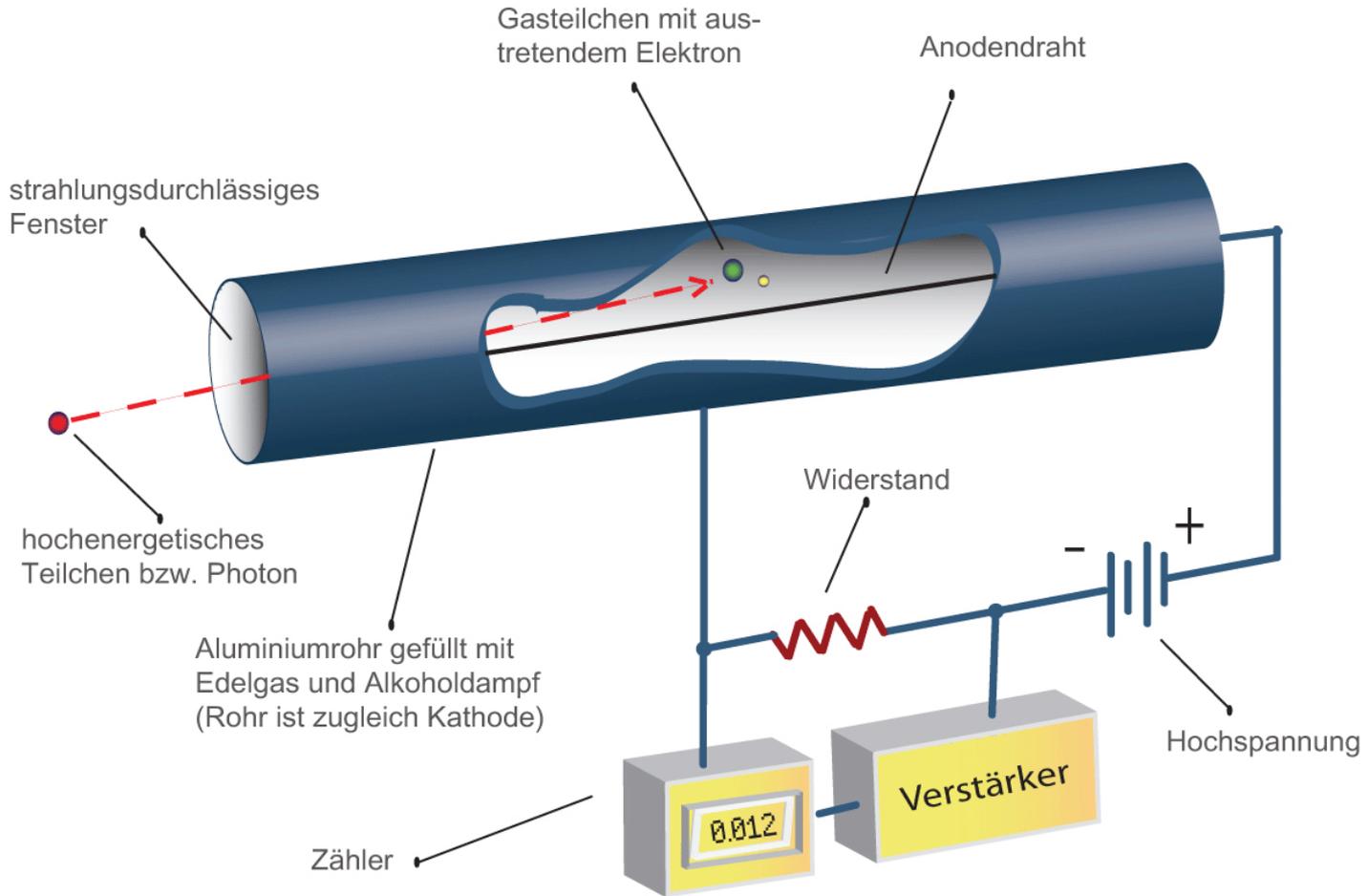


X-ray tube



X-ray tube with shielding

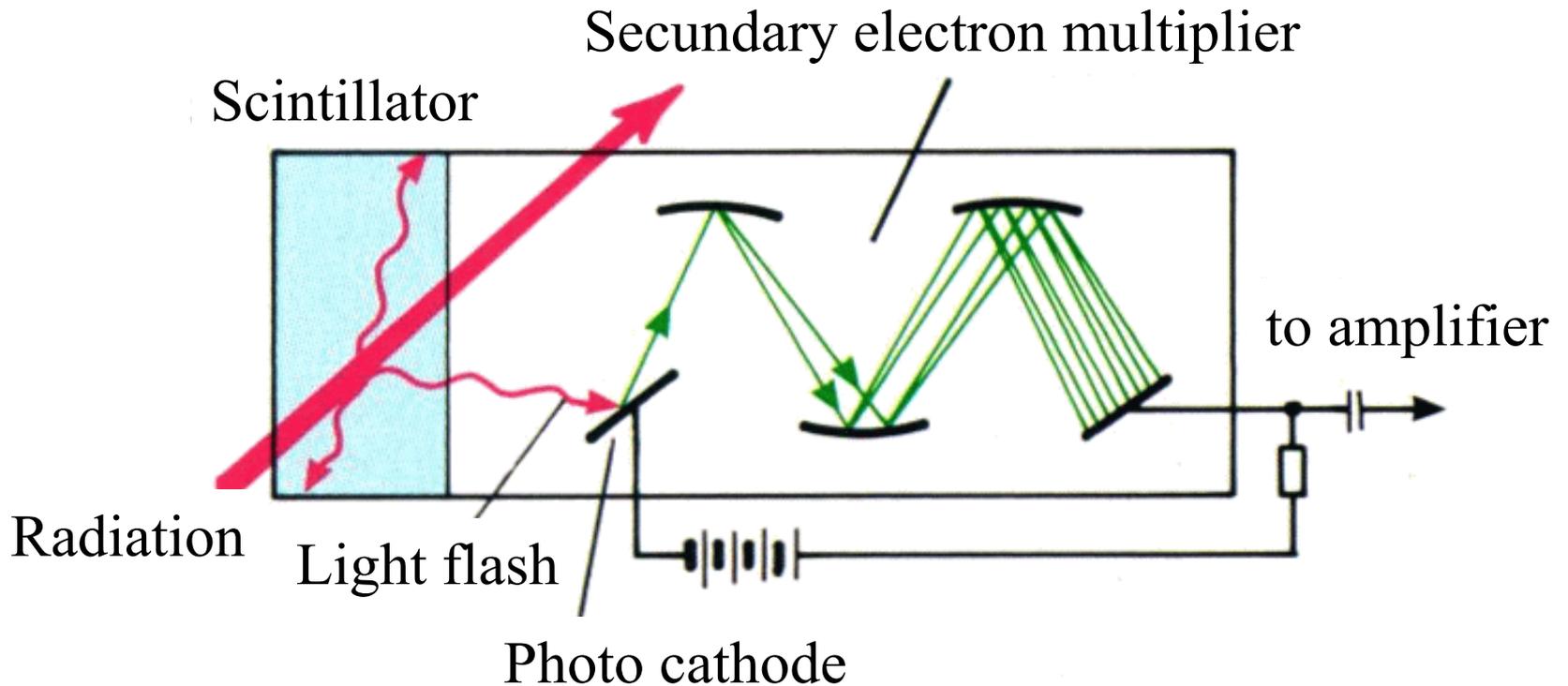
# X-Ray Detectors



Classical detector: Geiger-Müller Counter

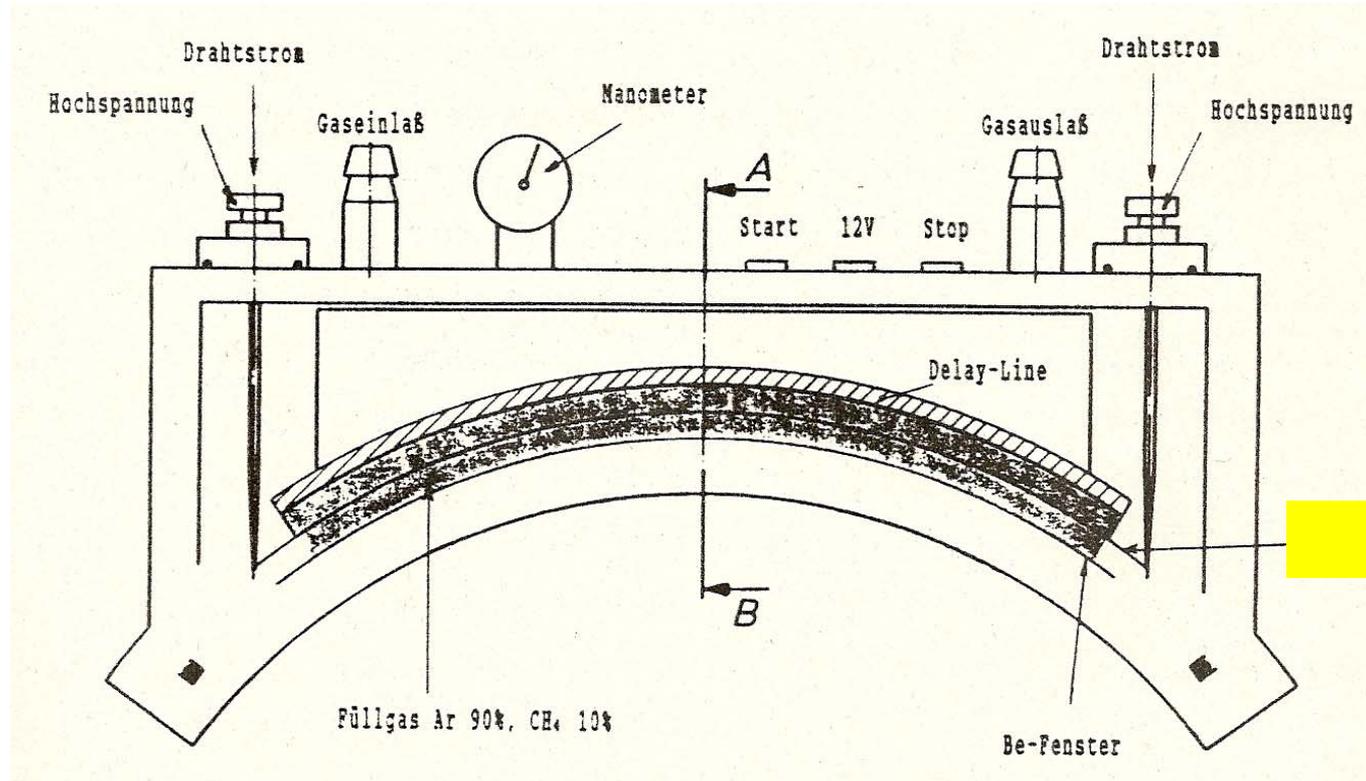
# X-Ray Detectors

Scintillation counter



Modern detector: Scintillation counter

# X-Ray Detectors

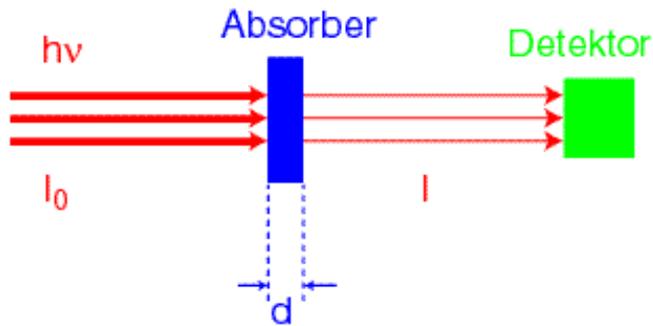


## Modern site-sensitive Detector

One or two dimensional detection of angle or direction of X-rays are diffracted to

# Absorption of X-Rays

- Reduction by absorber



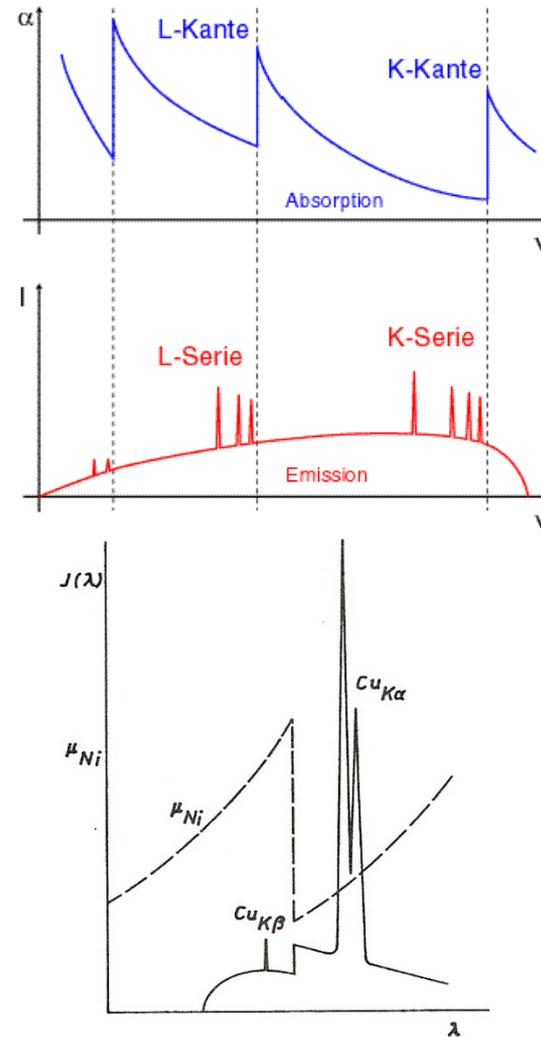
$$I = I_0 \cdot e^{-\alpha d}$$

- Absorptionskoeffizient  $\alpha$
- Halbwertsdicke

$$d_{\frac{1}{2}} = \alpha^{-1} \cdot \ln(2)$$

Absorption of X-rays

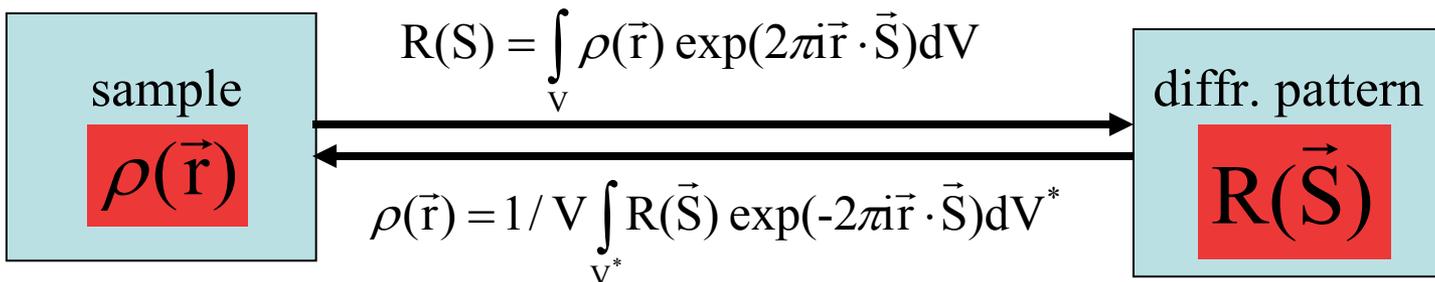
- Spectrum: Absorption edges



Filtering effects of a Ni-Foil for  $\text{Cu-K}_{\alpha}$  radiation (monochromating) <sup>12</sup>

# Scattering/Diffraction of X-rays

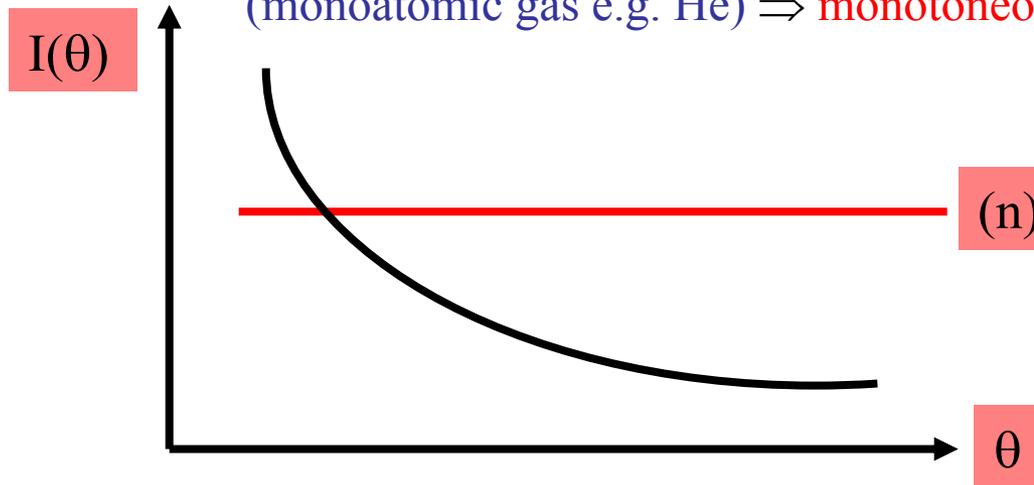
If a substance is irradiated by electromagnetic Radiation or neutrons of suitable wavelengths, a small part of the primary radiation ( $\sim 10^{-6}$ ) is scattered by the electrons or nuclei of the atoms or ions or molecules of the sample **elastically** ( $\Delta E = 0$ ) and **coherently** ( $\Delta\phi = \text{konstant}$ ) in all directions. The resulting **scattering/diffraction pattern**  $\mathbf{R}$  is the **Fourier transform** of the **electron/scattering distribution function**  $\rho$  of the sample and vice versa.



The shape of the resulting **scattering/diffraction pattern** depends on the **degree of order** of the sample.

# A. X-ray Scattering Diagram of an Amorphous Sample

no long-range order, no short range order  
 (monoatomic gas e.g. He)  $\Rightarrow$  **monotoneous decrease**

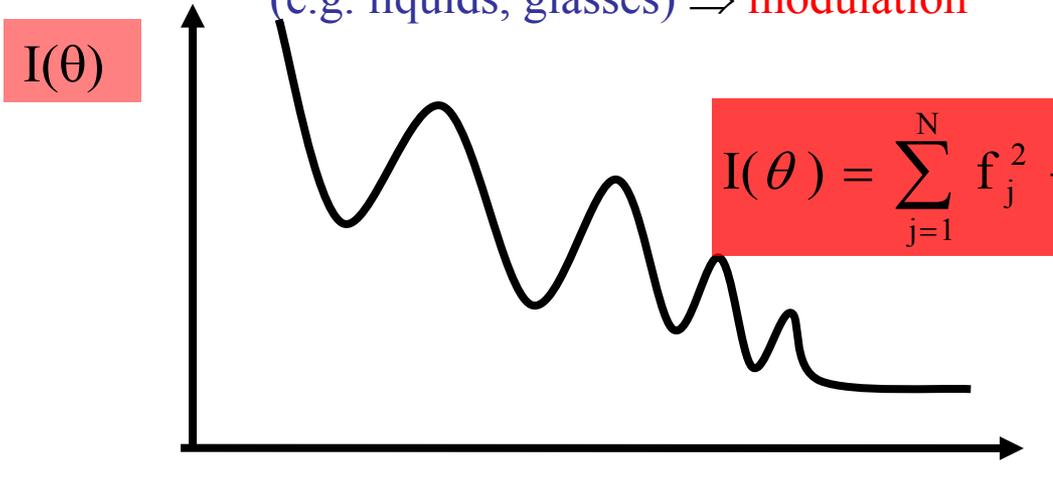


$$I(\theta) = N \cdot f^2$$

$f$  = scattering length of atoms  $N$

$\Rightarrow$  no information

no long-range, but short range order  
 (e.g. liquids, glasses)  $\Rightarrow$  **modulation**

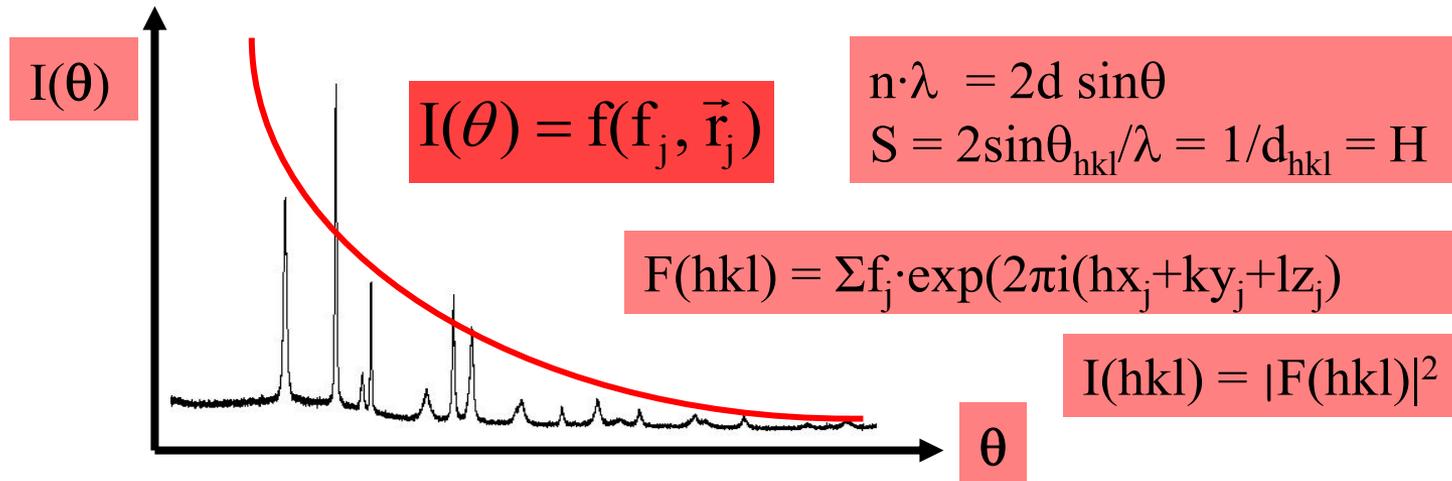


$$I(\theta) = \sum_{j=1}^N f_j^2 + 2 \sum_{j>} \sum_i f_j f_i \cos \left[ \pi (\vec{r}_j - \vec{r}_i) \vec{S} \right]$$

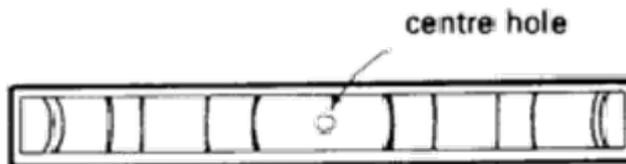
$\Rightarrow$  radial distribution function  
 atomic distances

## B. X-ray Scattering Diagram of a Crystalline Sample

crystals and crystal powders have long-range and short-range order  
 $\Rightarrow$  discontinuous scattering diagrams with discrete reflections



crystal powder  
 orientation statistical,  $\lambda$  fixed  
 $\Rightarrow$  cones of interference



Debye-Scherrer diagram

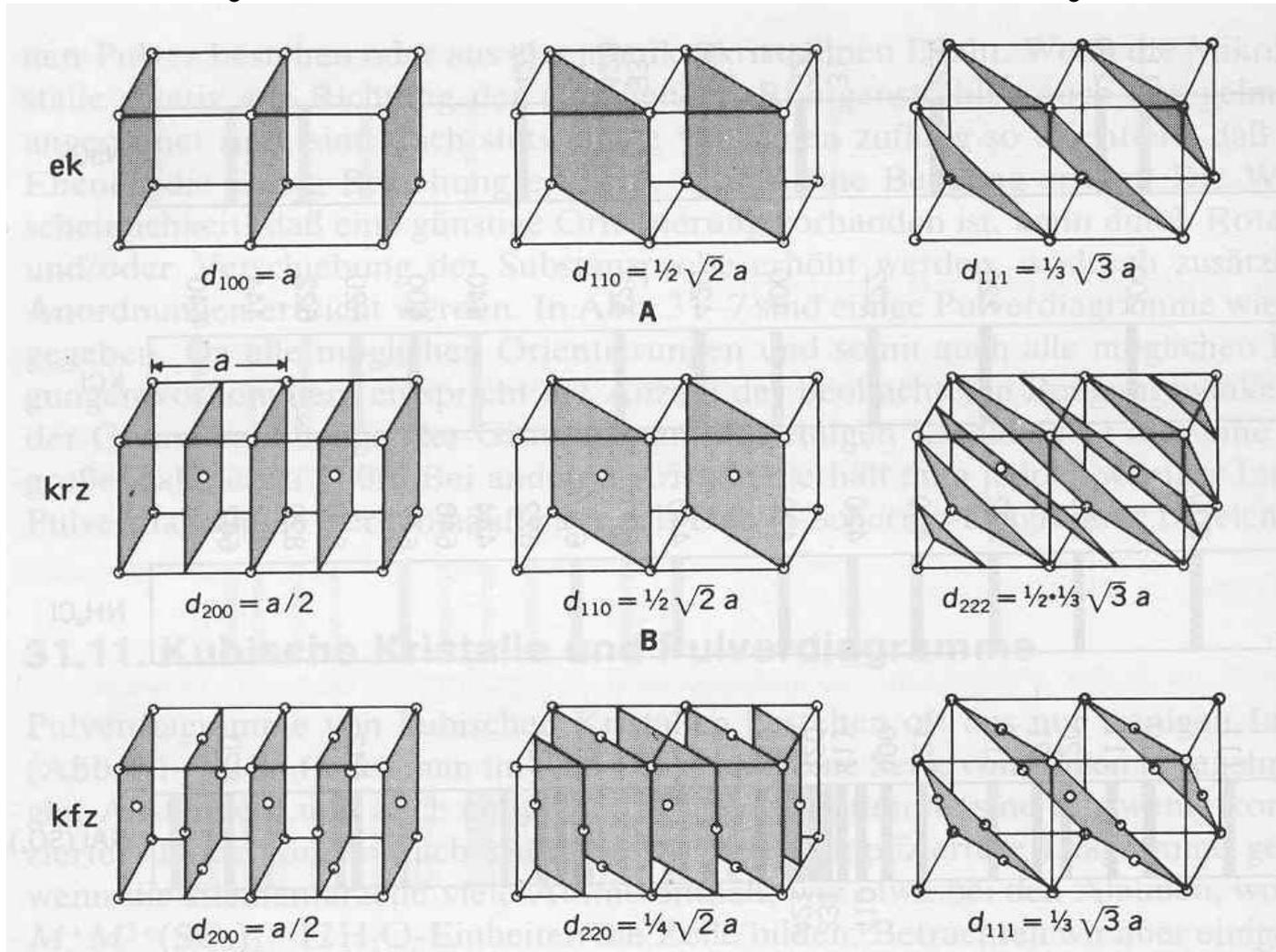
single crystal  
 orientation or  $\lambda$  variable  
 $\Rightarrow$  dots of interference (reflections)



precession diagram

Why that?

# Atoms in crystals are three-dimensionally ordered

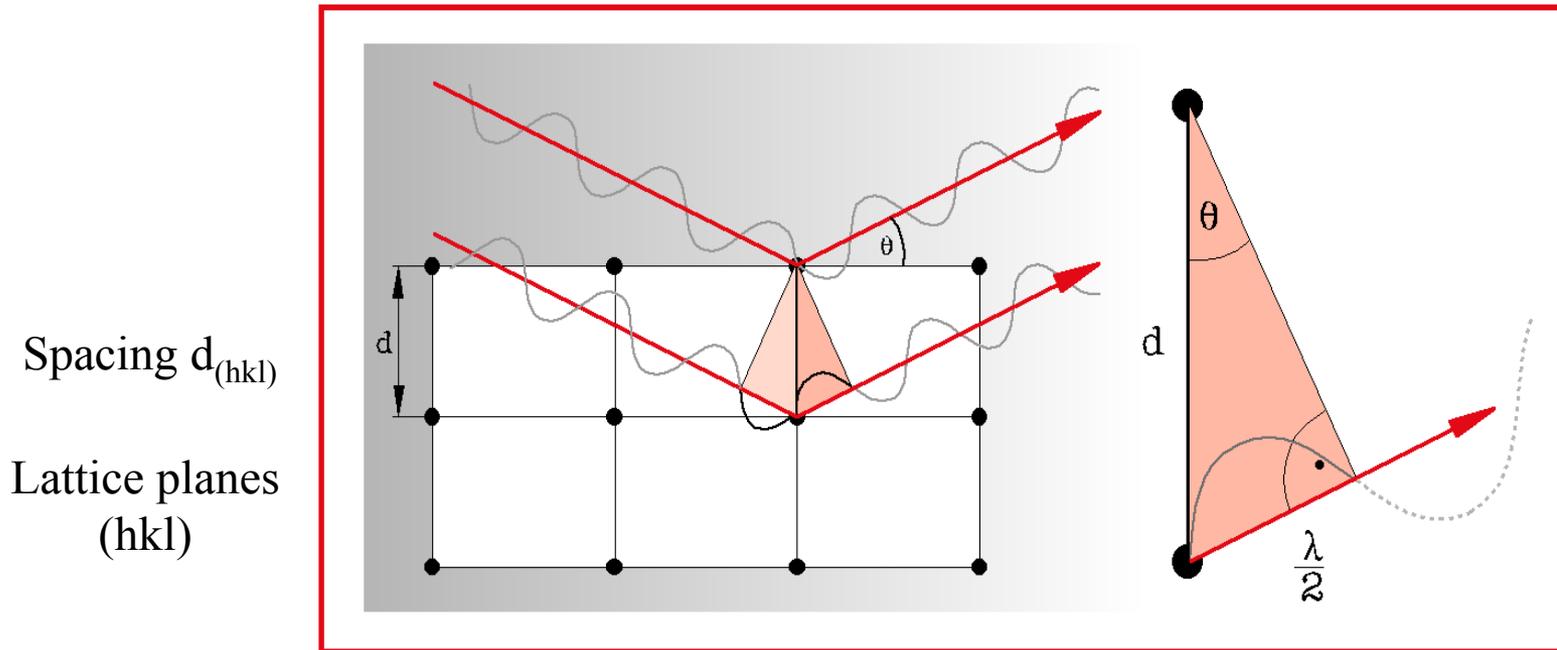


forming lattice plane families (Miller indices  $hkl$ , spacings  $d_{hkl}$ )

# Diffraction of X-rays (neutrons, electrons!) by a Crystalline Sample (Single Crystal or Crystal Powder)

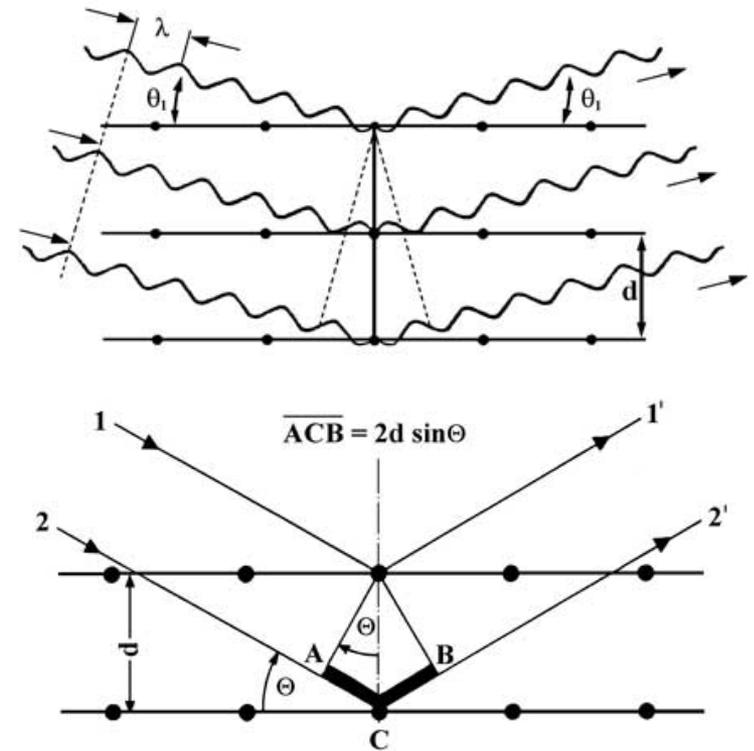
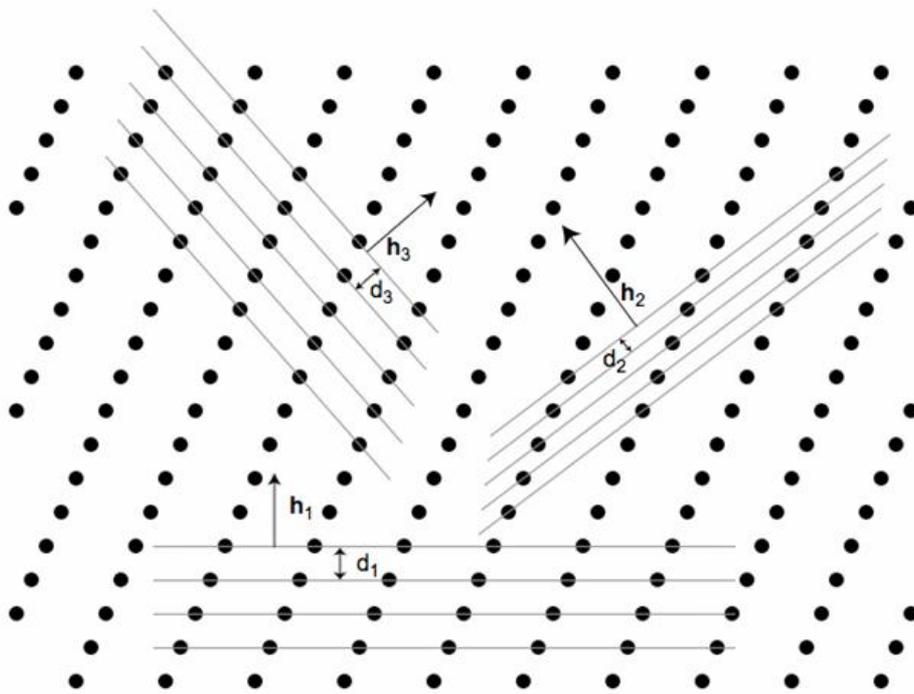
X-rays scattered by a crystalline sample are not totally extinct only for those directions, where the scattered rays are „in phase“.

$R(S)$  und  $I(\theta)$  therefore are periodic functions of „Bragg reflections“.



$$\text{Bragg equation: } n \cdot \lambda = 2d \cdot \sin\theta \text{ or } \lambda = 2d_{(hkl)} \cdot \sin\theta_{(hkl)}$$

# Diffraction of X-rays by crystalline samples



Directions and planes of a regular lattice with Miller indices  $hkl$  and spacings  $d_{hkl}$

Bragg equation:

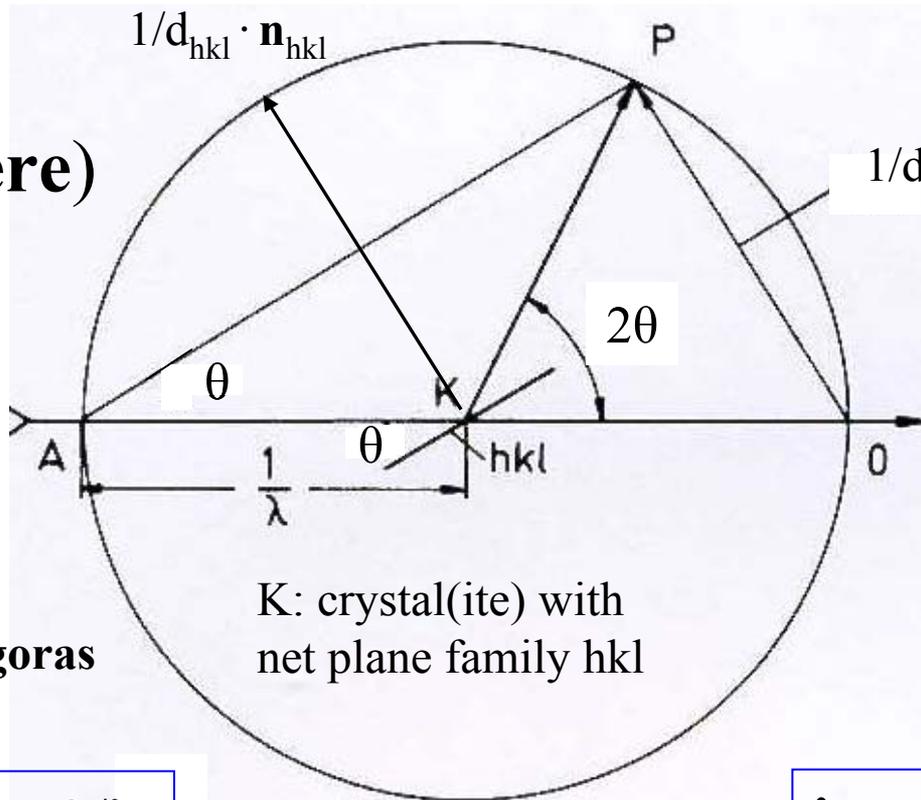
$$n\lambda = 2d \sin\theta$$

$$\lambda = 2d_{(hkl)} \sin\theta_{(hkl)}$$

# X-ray Diffraction (XRD)

(Ewald sphere)

primary beam



$1/d_{hkl} \cdot \mathbf{n}_{hkl}$

$\mathbf{n}$  = net plane (family)  
normal vector

primary beam

Theorem of Thales

Theorem of Pythagoras

K: crystal(ite) with  
net plane family  $hkl$

$$\sin\theta_{hkl} = 1/d_{hkl} \cdot 2/\lambda$$

**Bragg equation**

$$\lambda = 2d_{hkl} \cdot \sin\theta_{hkl}$$

The crystal or crystallite is positioned at the center of a (virtual) sphere of radius  $1/\lambda$  and is hit by a X-ray beam with wave length  $\lambda$  running along a center line of that sphere.

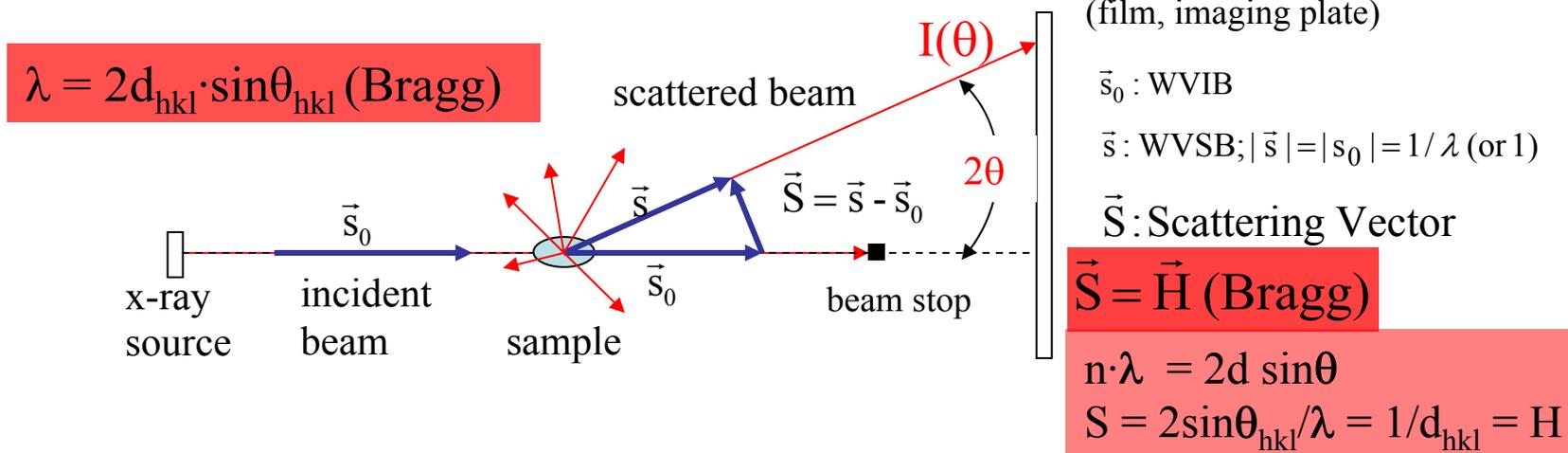
# **X-ray Diffraction (XRD)**

Reciprocal lattice

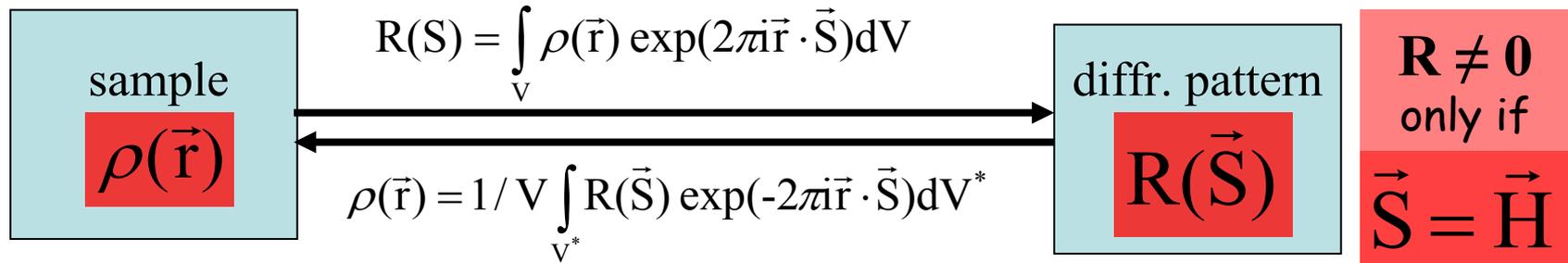


# (X-ray) Diffraction of a Crystalline Sample

(Single Crystal or Crystal Powder) detector



Fourier transform of the electron density distribution



$V$  : volume of sample  $\vec{r}$  : vector in space  $R$  : scattering amplitude

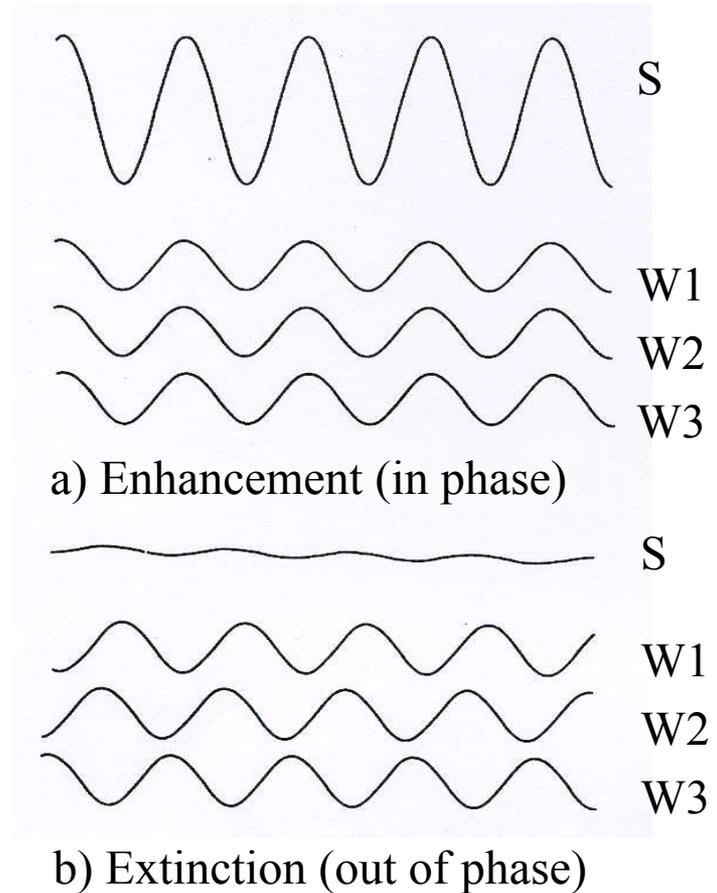
$\vec{S}$  : scattering vector  $\equiv$  vector in Fourier (momentum) space

# X-ray Powder Diffraction (XRPD)

Superposition (interference) of the X-rays scattered by the **electrons of the atoms** results in enhancement (a) or extinction (b) of the X-rays.

- X-rays scattered by an atom are described by the **atomic scattering or form factor  $f_j$** .

- X-rays scattered by all atoms of a unit cell of a crystal are described by the **structure factor  $F_{hkl}$** .

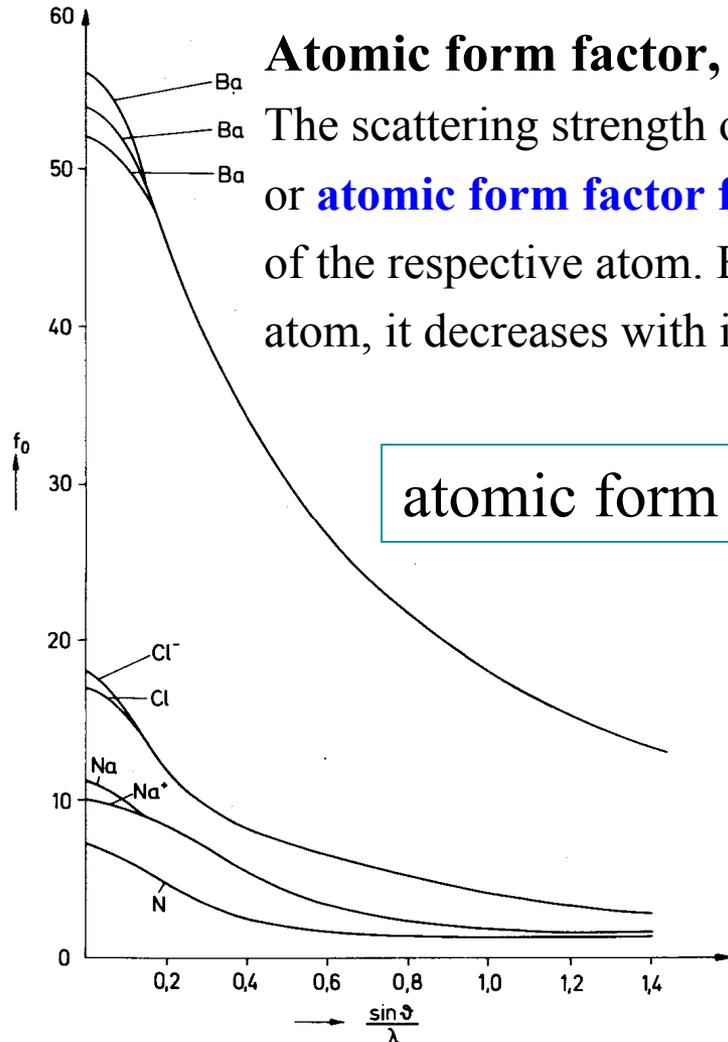


## Superposition (interference) of X-rays

# X-ray Powder Diffraction (XRPD)

## Atomic form factor, scattering strength of atoms

The scattering strength of an atom  $j$  is described by the atomic scattering or **atomic form factor  $f_j$** . It is proportional to the number of electrons of the respective atom. Because of the size of the electron cloud of an atom, it decreases with increasing scattering angle.



atomic form factor  $f_j(\theta = 0) \equiv$  order number  $Z_j$

For the correction of enlargement of the electron cloud by thermal motion the Debye-Waller factor is used:

$$f_j = f_{j0} \exp(-B \sin^2 \theta / \lambda^2)$$

Scattering strength  $f_{j0}$  of a non-vibrating single atom (atomic form factor, atomic scattering factor) as a function of  $\sin \theta / \lambda$

# X-ray Powder Diffraction (XRPD)

## Structure factor $F_{hkl}$

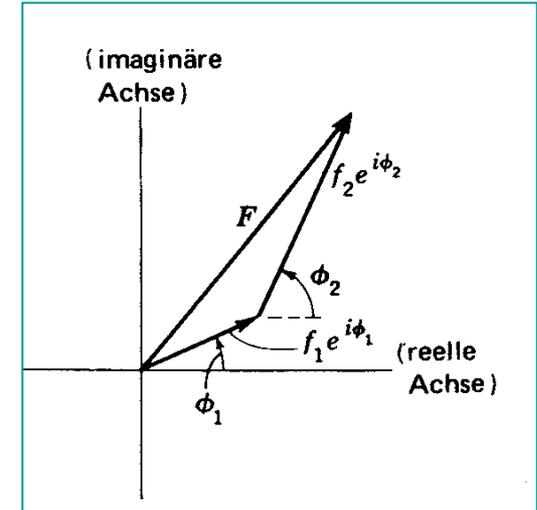
The scattering power of **all** atoms of an unit cell of a crystal is characterized by the so called **structure factor  $F_{hkl}$** . It is (for  $\theta = 0$ ) proportional to the sum of the scattering contributions of all the atoms of the unit cell.  $F_{hkl}$  is characteristic for every family of lattice planes (hkl) and in general a complex number. In a unit cell with n atoms, the structure factor is:

$$F_{hkl} = \sum_{j=1}^n f_j \exp [2\pi i (hx_j + ky_j + lz_j)]$$

h,k,l: Miller indices,  $x_j, y_j, z_j$ : atomic positional coordinates.

Using the **Euler equation**  $\exp(i\varphi) = \cos\varphi + i \sin\varphi$ , the structure factor becomes:

$$F_{hkl} = \sum f_j \cos 2\pi(hx_j + ky_j + lz_j) + i \sum f_j \sin 2\pi(hx_j + ky_j + lz_j)$$



Measurable is only the intensity, i.e. the square of the structure amplitude:  $I_{hkl} \sim F_{hkl}^2$ . This means that all the phases of the complex numbers  $F_{hkl}$  (or the signs in case of centrosymmetric crystal structures) are lost.

≡ „Phase problem of crystal structure analysis/determination“

# X-ray Powder Diffraction (XRPD)

## Structure factor $F_{hkl}$

If the structure has a center of symmetry (centrosymmetric structure), the structure factor

$$F_{hkl} = \sum f_j \cos 2\pi(hx_j + ky_j + lz_j) + i \sum f_j \sin 2\pi(hx_j + ky_j + lz_j)$$

reduces/simplifies by compensation/elimination of the imaginary parts to

$$F_{hkl} = \sum f_j \cos 2\pi(hx_j + ky_j + lz_j),$$

thus the „**phase problem**“ reduces to a „**sign problem**“.

## Structure amplitude $F_{hkl} = |F_{hkl}|$ and Scattering intensity $I_{hkl}$

The **modulus of the structure factor** is named **scattering** or **structure amplitude**.

The **scattering intensity** is proportional to the square of the structure amplitude:  $I_{hkl} \sim |F_{hkl}|^2$ .

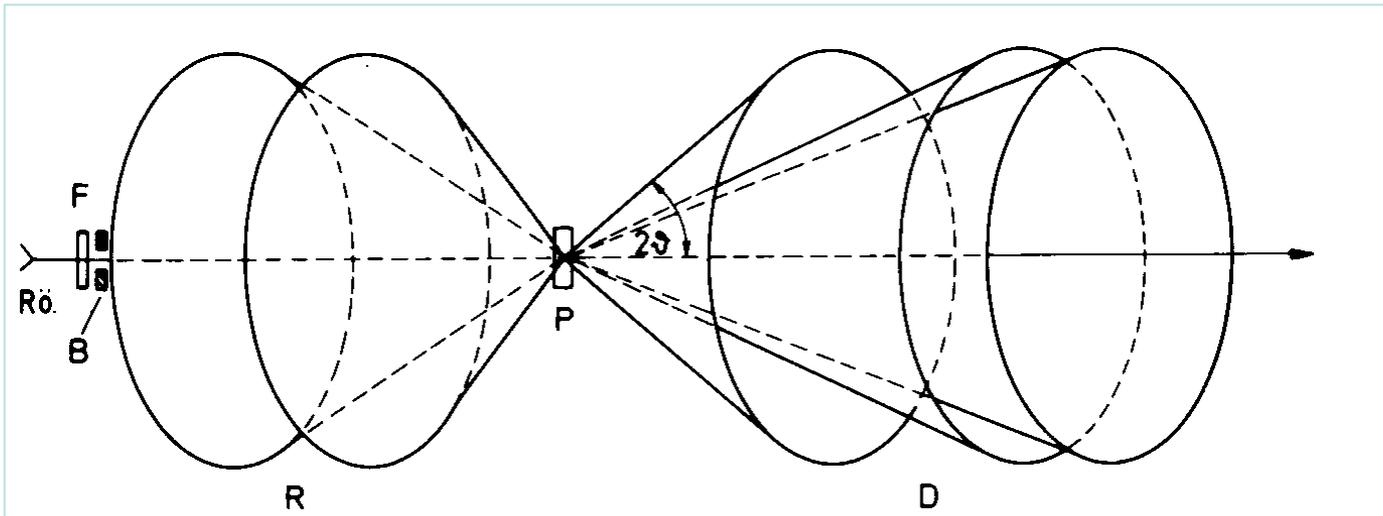
The **structure amplitudes** can be calculated (after correction for absorption, extinction, and Lorentz-polarisation effects) from the intensities  $I_{hkl}$  ( $\rightarrow$  **data reduction**):

$$I_{hkl} = K \cdot F \cdot A \cdot E \cdot Lp \cdot |F_{hkl}|^2$$

(K = scale factor, F = coincidence factor, A = absorption factor, E = extinction factor, Lp = Lorentz-polarisation factor)

# X-ray Powder Diffraction (XRPD)

In a powder sample all crystallites are statistically (randomly) oriented. Thus a powder sample produces for each family of lattice planes **hkl** a distinct scattering cone of high intensity



The cone angle is  **$4\theta_{hkl}$**  (4 x the scattering angle  $\theta_{hkl}$ )

With the scattering angle  **$\theta_{hkl}$** , the lattice plane distance  **$d_{hkl}$**  of the respective family of lattice planes can be calculated by use of the Bragg equation ( $\lambda$  = wave length):

$$d_{hkl} = \lambda / (2 \sin \theta_{hkl}).$$

# X-ray Powder Diffraction (XRPD)

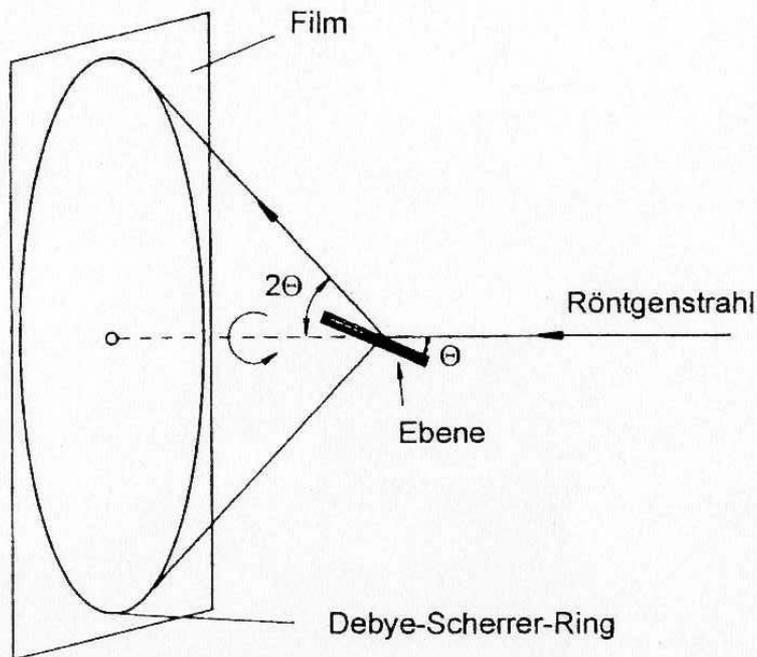
Diffraction cones (reflections) with randomly or symmetry-caused identical d values fall together leading to symmetry-caused coincidences → **Net plane occurrence factor**

Flächenhäufigkeitsfaktoren für Pulververfahren

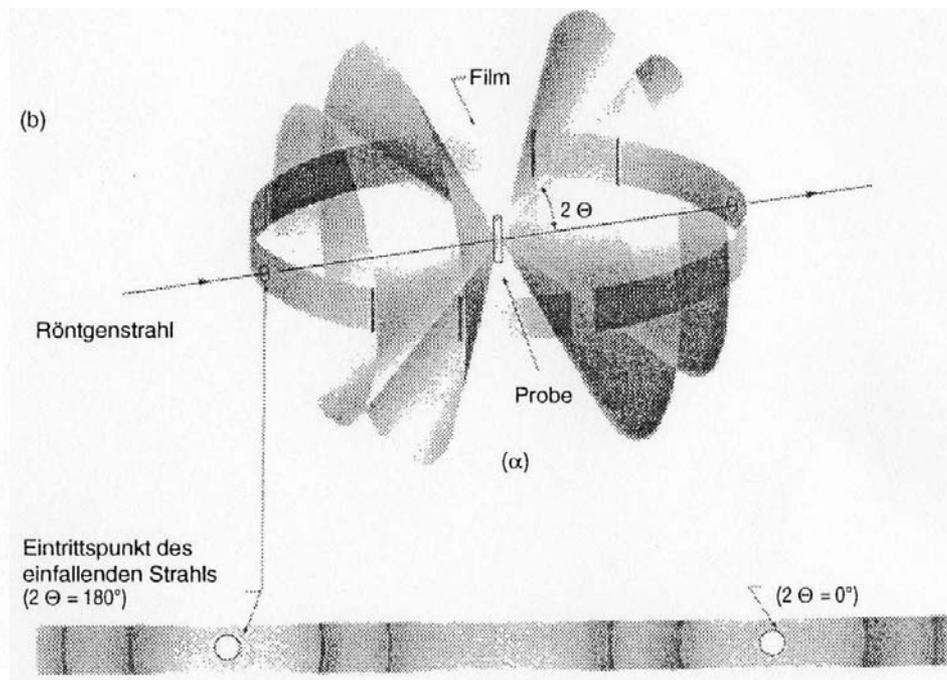
<i>hkl</i>	kubisch	tetrag.	hexagonal	rhombisch	monoklin	triklin
<i>hkl</i>	48	16	24	8	4	2
<i>hhl</i>	24	8	12	8	4	2
<i>hlh</i>	24	16	24	8	4	2
<i>lhh</i>	24	16	24	8	4	2
<i>hk0</i>	24	8	12	4	2	2
<i>h0l</i>	24	16	12	4	4	2
<i>0kl</i>	24	16	12	4	4	2
<i>hhh</i>	8	8	12	8	4	2
<i>hh0</i>	12	4	6	4	2	2
<i>h0h</i>	12	8	12	4	4	2
<i>0hh</i>	12	8	12	4	4	2
<i>h00</i>	6	4	6	2	2	2
<i>0k0</i>	6	4	6	2	2	2
<i>00l</i>	6	2	2	2	2	2

# X-ray Powder Diffraction (XRPD)

## Debye-Scherrer geometry



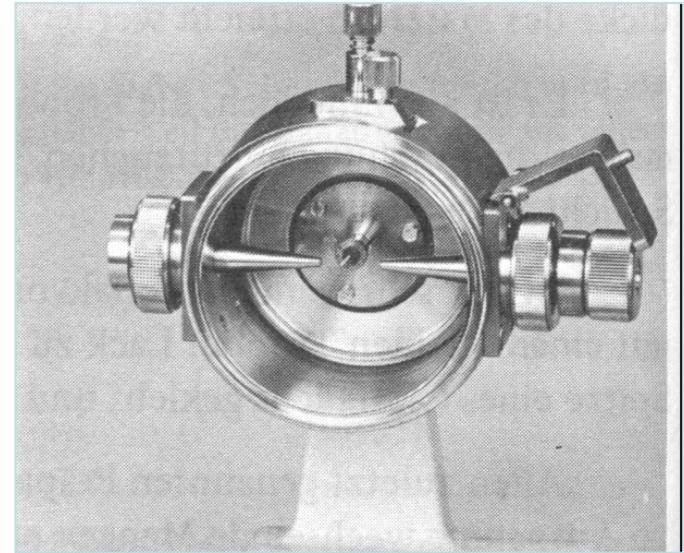
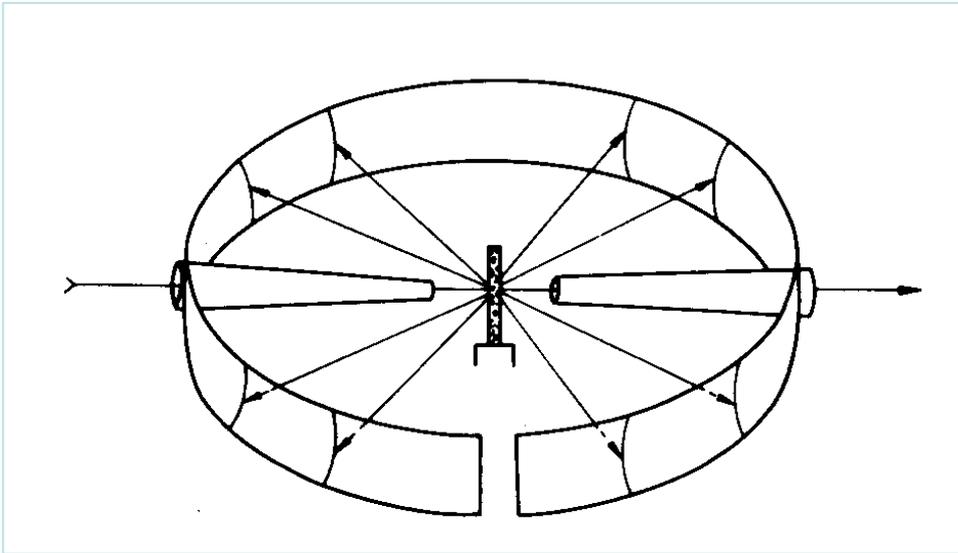
Debye-Scherrer pattern  
using a flat film



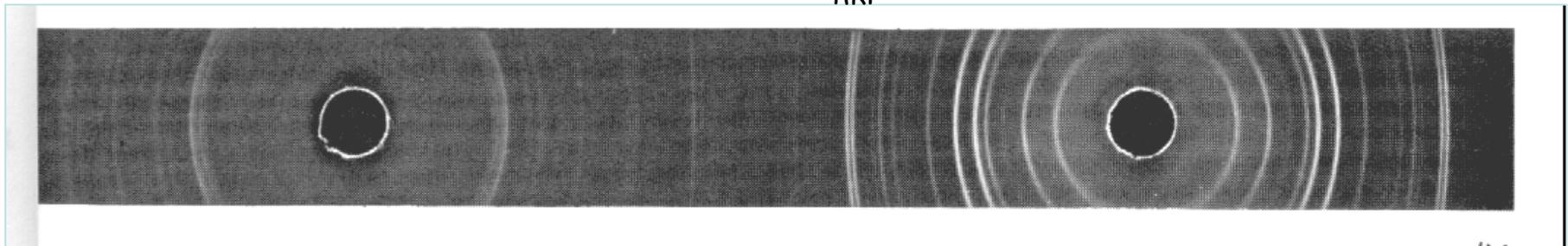
Debye-Scherrer pattern  
using a cylindric film

# X-ray Powder Diffraction (XRPD)

Debye-Scherrer geometry



$$\leftarrow \text{---} 180^\circ \geq 2\theta_{hkl} \geq 0^\circ \text{---} \rightarrow$$

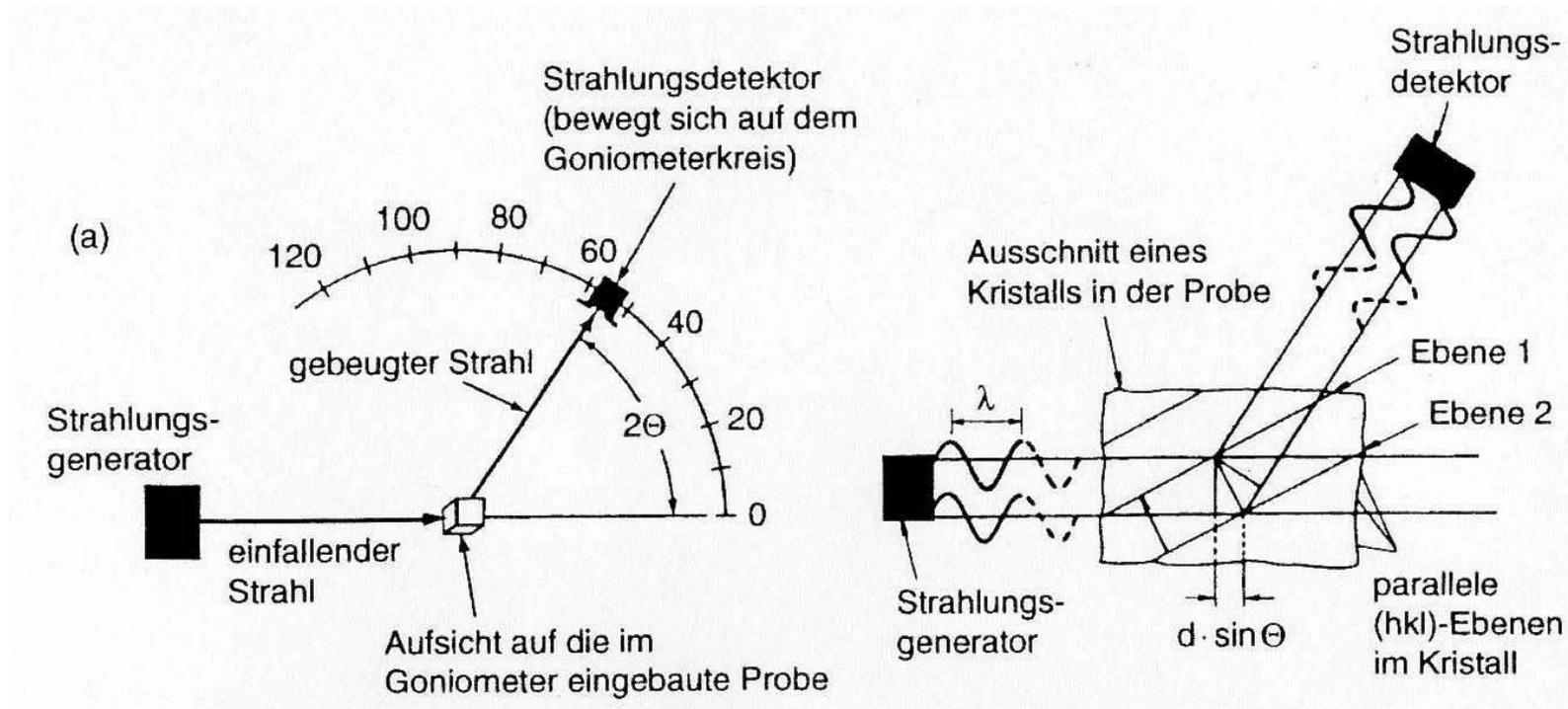


$$\leftarrow 360-4\theta_{hkl} \rightarrow$$

$$\leftarrow 4\theta_{hkl} \rightarrow$$

# X-ray Powder Diffraction (XRPD)

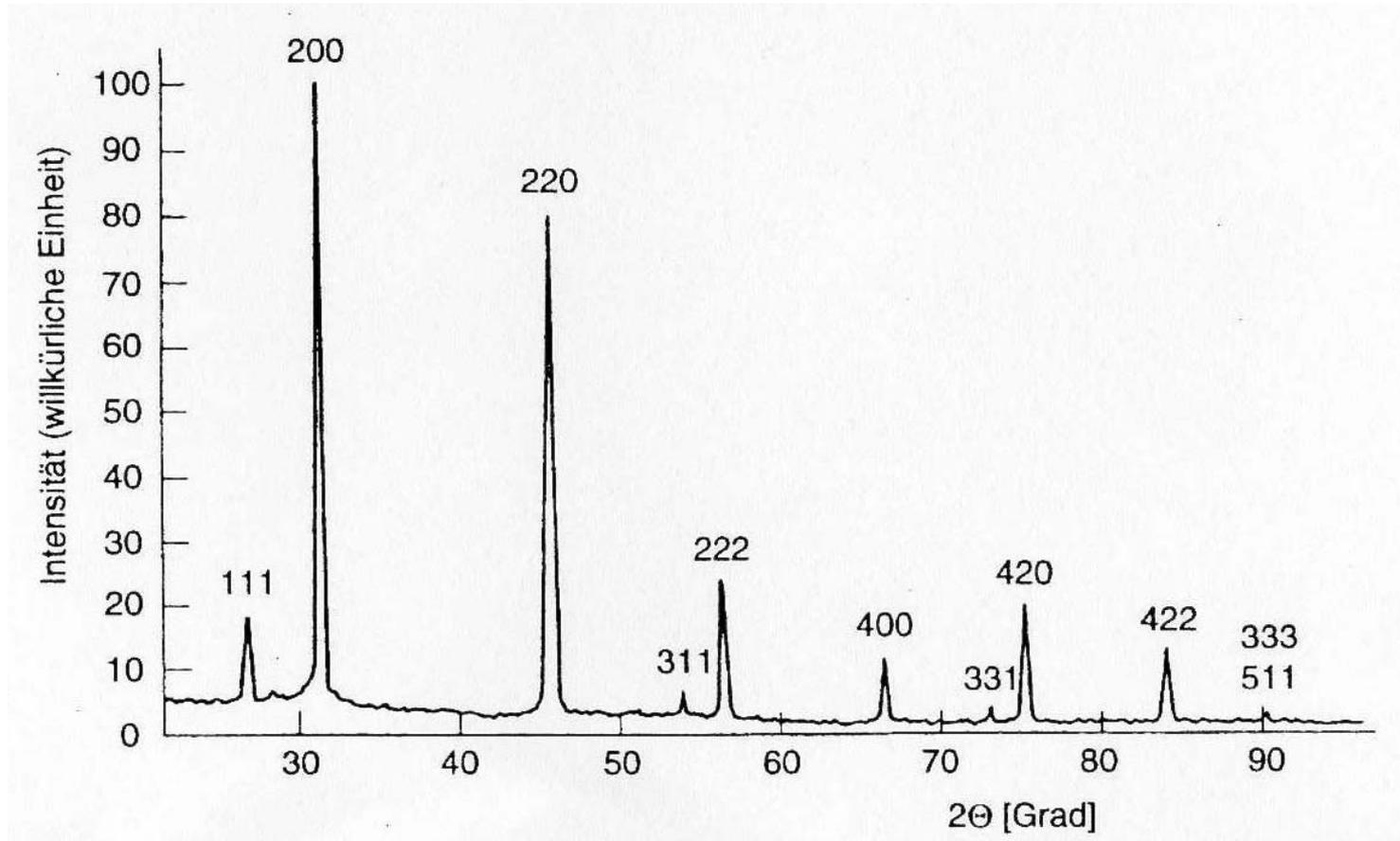
## X-ray powder diffractometer



X-ray powder diffractometer and scattering geometry of/in a sample

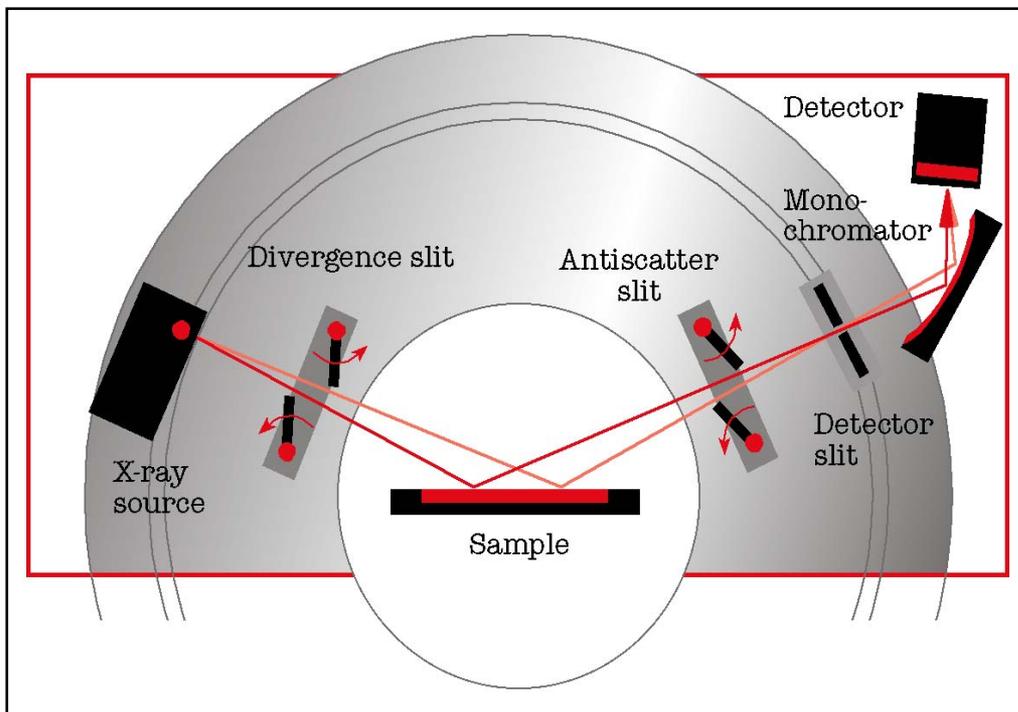
# X-ray Powder Diffraction (XRPD)

X-ray powder diffractometer



X-ray diffraction pattern of a powder sample

# X-ray Powder Diffraction (XRPD)

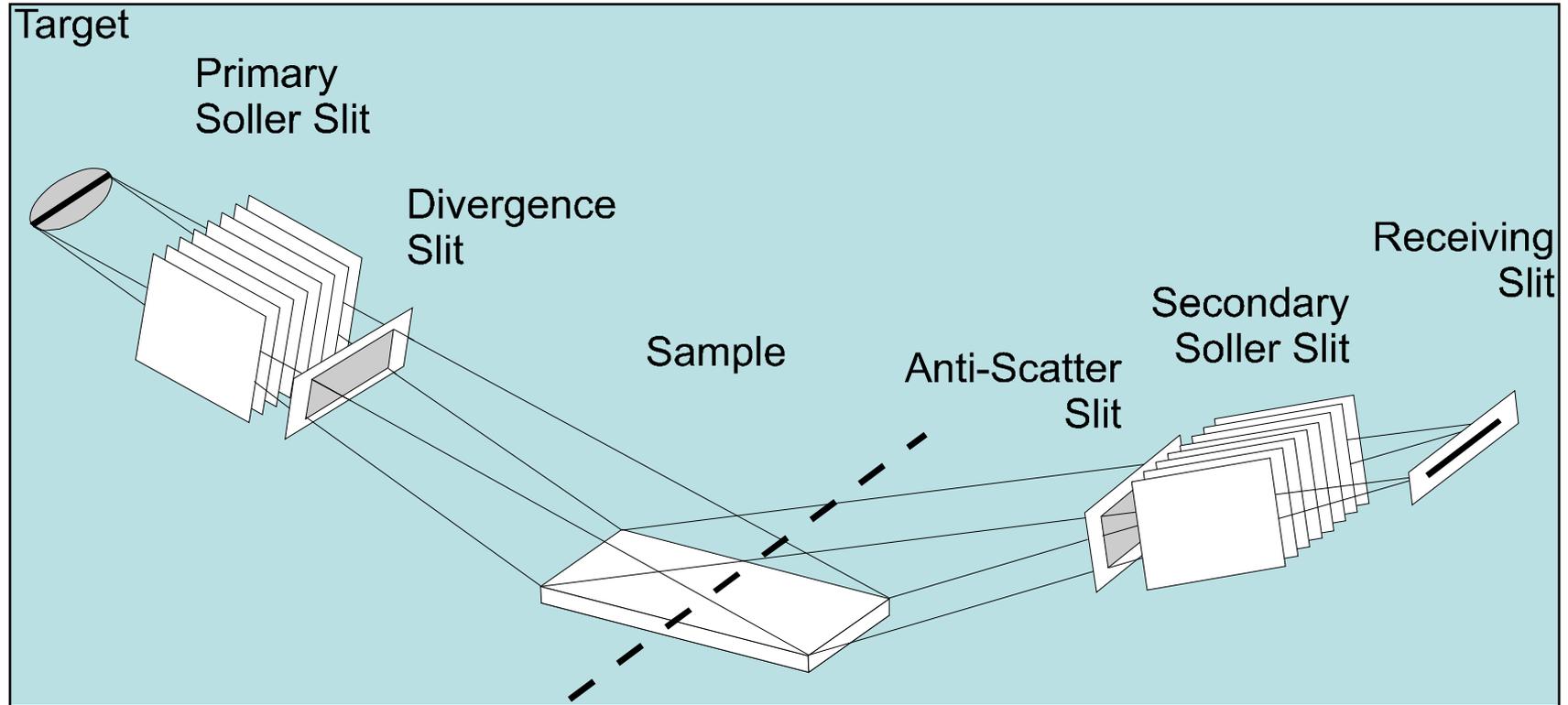


## Powder diffractometer with Bragg-Brentano geometry

Normal of the sample bisects the angle between primary and diffracted beam directions.

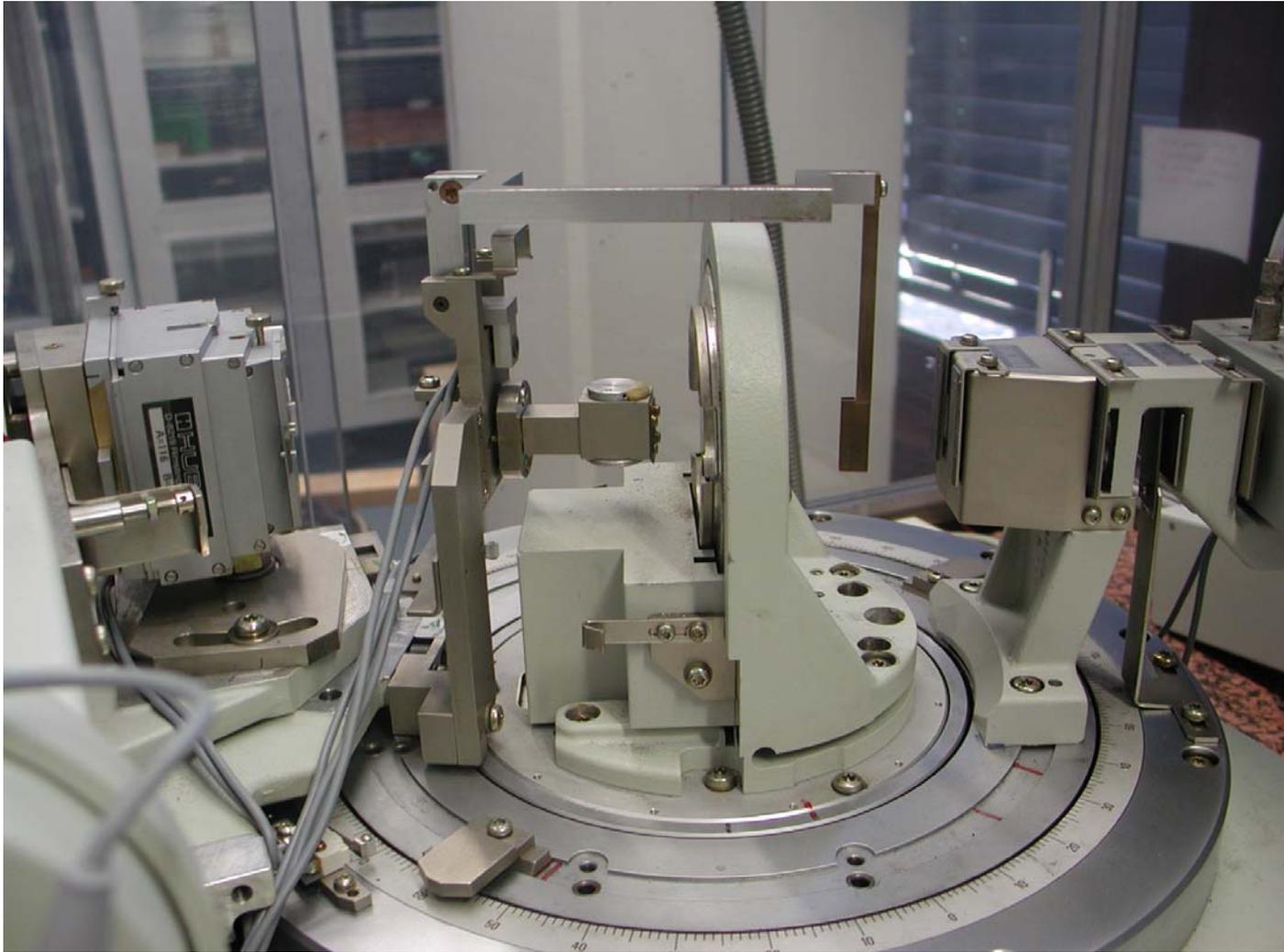
- Sample is fixed, tube and detector turn to each other by an angle  $\theta$ .
- Tube is fixed, sample and detector turn by an angle  $\theta$ , and  $2\theta$ , respectively in the same direction.

# X-ray Powder Diffraction (XRPD)



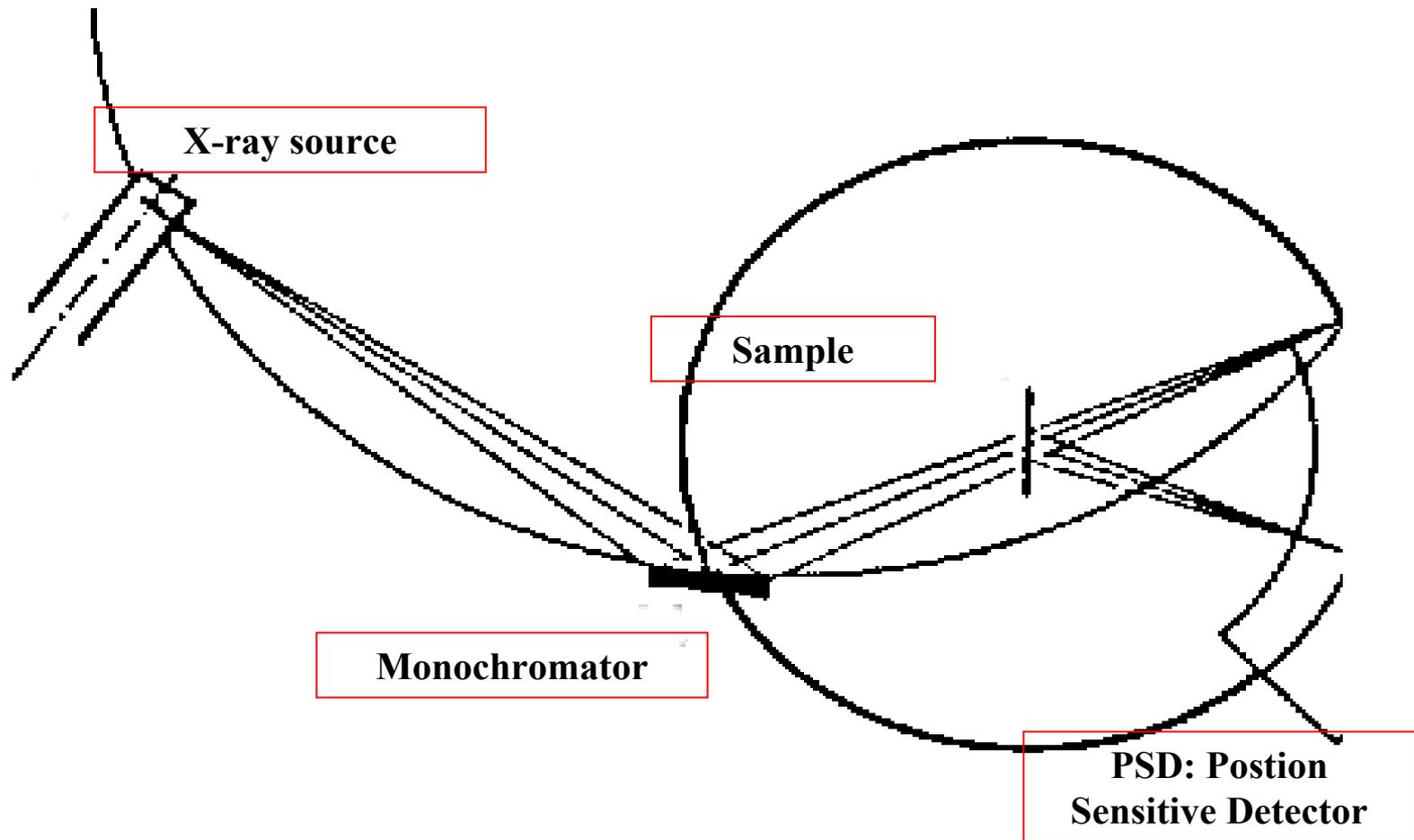
Beam course for the Bragg-Brentano geometry

# X-ray Powder Diffraction (XRPD)



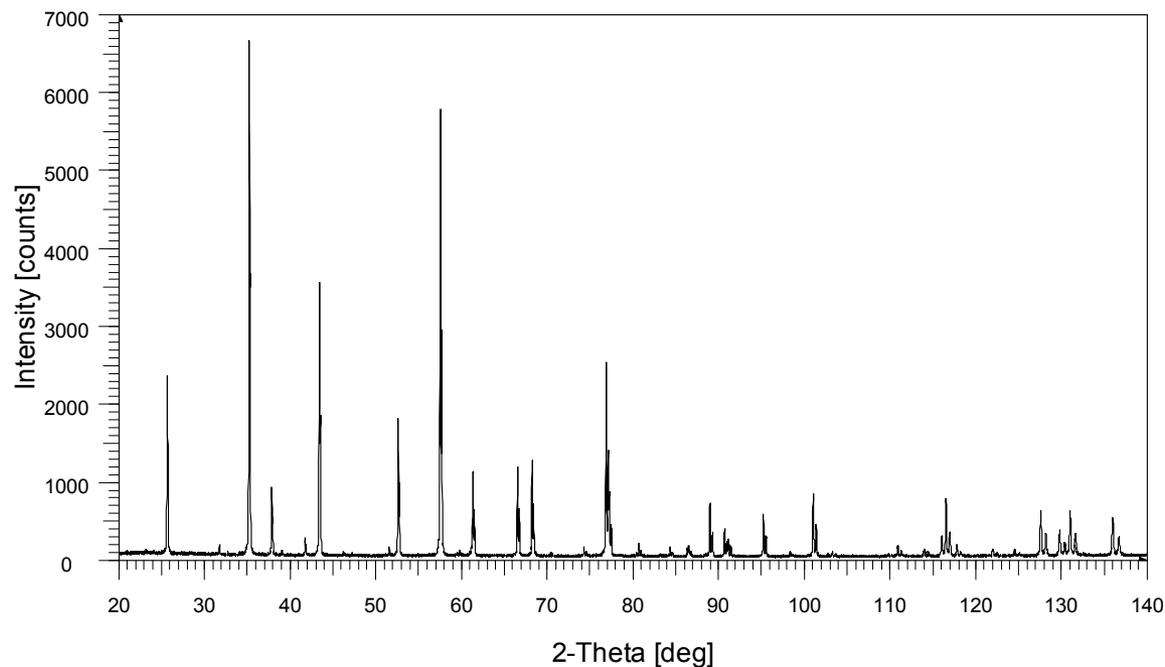
Powder Diffractometer Bruker AXS D 5000

# X-ray Powder Diffraction (XRPD)



Schematic diagram of the beam course in a powder diffractometer with a focusing monochromator and PS detector

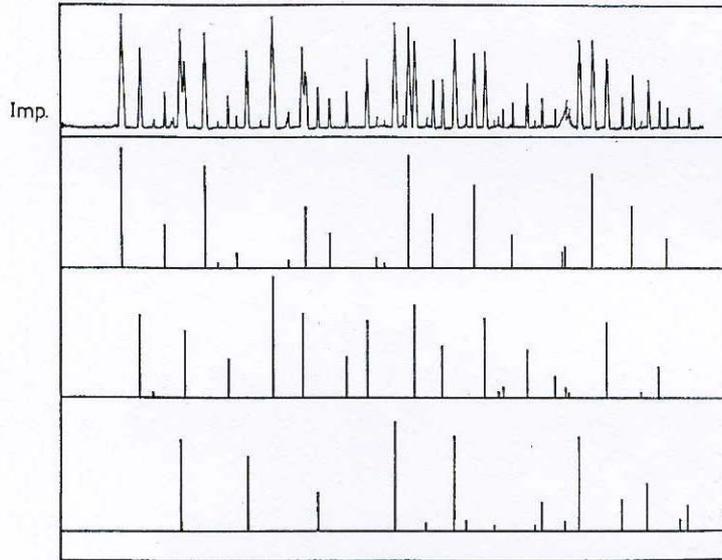
# X-ray Powder Diffraction (XRPD)



- **D8 ADVANCE,**
- **Cu-Strahlung,**  
**40 kV, 40 mA**
- **Schrittweite: 0,013°**
- **Zeit pro Schritt:**  
**0,02 sec**
- **Geschwindigkeit:**  
**39°/ Minute**
- **Totale Messzeit:**  
**3:05 Minuten**

Standard measurement in Bragg-Brentano geometry (corundum plate )

# X-ray Powder Diffraction (XRPD)



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Comparison with own data file

18-154

d	3.99	2.91	4.73	9.47	Ba(N <sub>3</sub> ) <sub>2</sub> ★					
1/1 <sub>1</sub>	100	80	70	20	Barium Azide					
Rad.	λ	Filter	Dia.	d Å	1/1 <sub>1</sub>	hkl	d Å	1/1 <sub>1</sub>	hkl	
Cutoff		Visual		9.47	20	001	2.295	40	211	
Ref. Tokar, Kirschner and Radl, Montash.Chem.96, 3, 932-40 (1965)				5.33	20	100	2.282	40	210	
				5.03	60	101	2.196	70	020,113	
				4.73	70	002	2.182	20	202	
				4.35	30	101	2.152	10	211	
Sys. Monoclinic		S.G.		3.99	100	011	2.083	30	014	
a <sub>0</sub> 5.42	b <sub>0</sub> 4.39	c <sub>0</sub> 9.59	A	3.39	60	110	2.046	10	114	
α	β 99.75°	γ	Z 2	3.27	20	102	2.030	10	120	
Ref. Ibid.			Dx 3.25	3.15	30	003	2.013	40	121	
				3.08	70	111	1.992	60	213,022	
εα	nωβ	εγ	Sign	2.943	20	103	1.961	30	121	
2V	D 3.22	mp	Color	2.909	80	112	1.952	30	212	
Ref. Ibid.				2.693	40	201	1.942	10	204	
				2.673	30	200	1.893	20	005,203	
				2.627	10	112	1.823	20	122	
				2.562	70	013	1.803	30	023	
				2.537	10	103				
				2.514	10	202				
				2.468	20	201				
				2.366	10	004				

FORM T-2

Comparison with JCPDS

Phase analysis or identification of a sample using XRPD  
(JCPDF = Joint Committee of Powder Diffraction File)

# X-ray Powder Diffraction (XRPD)

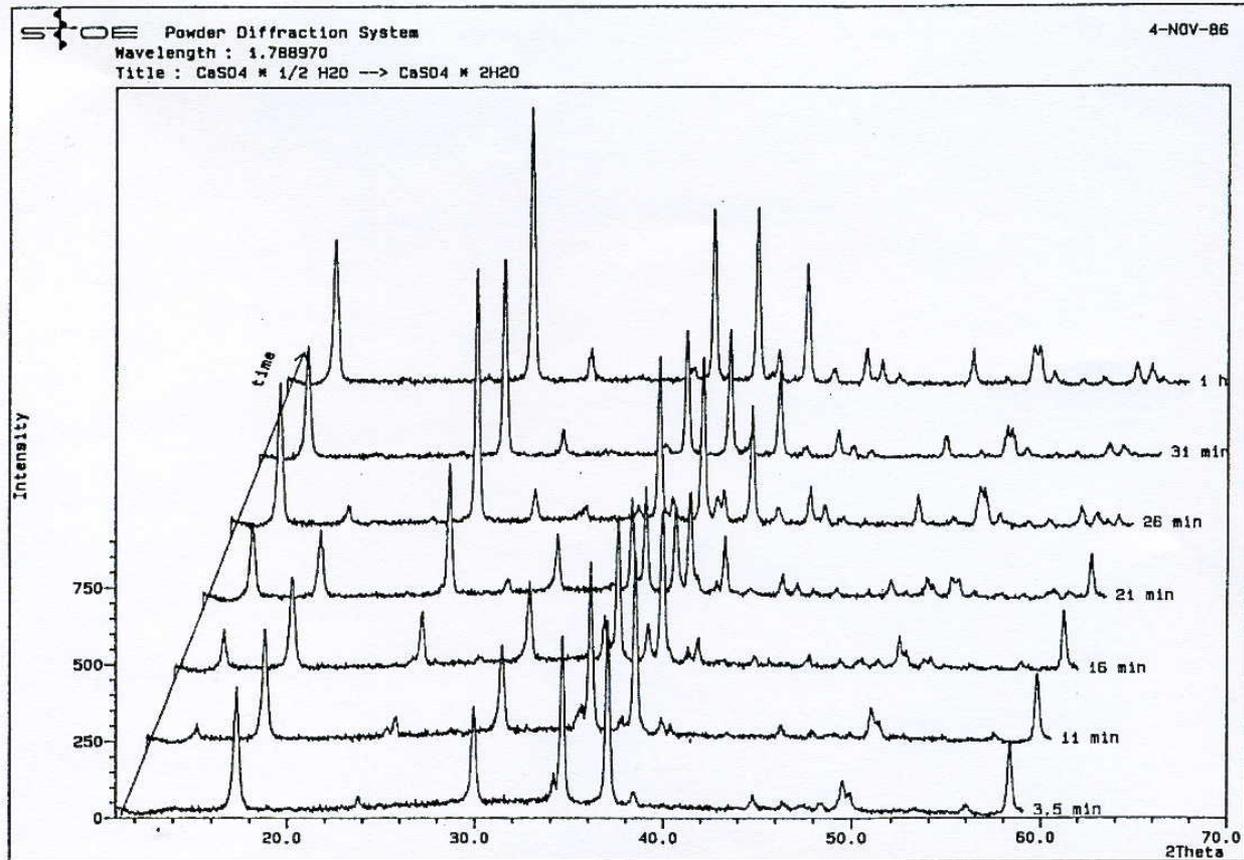
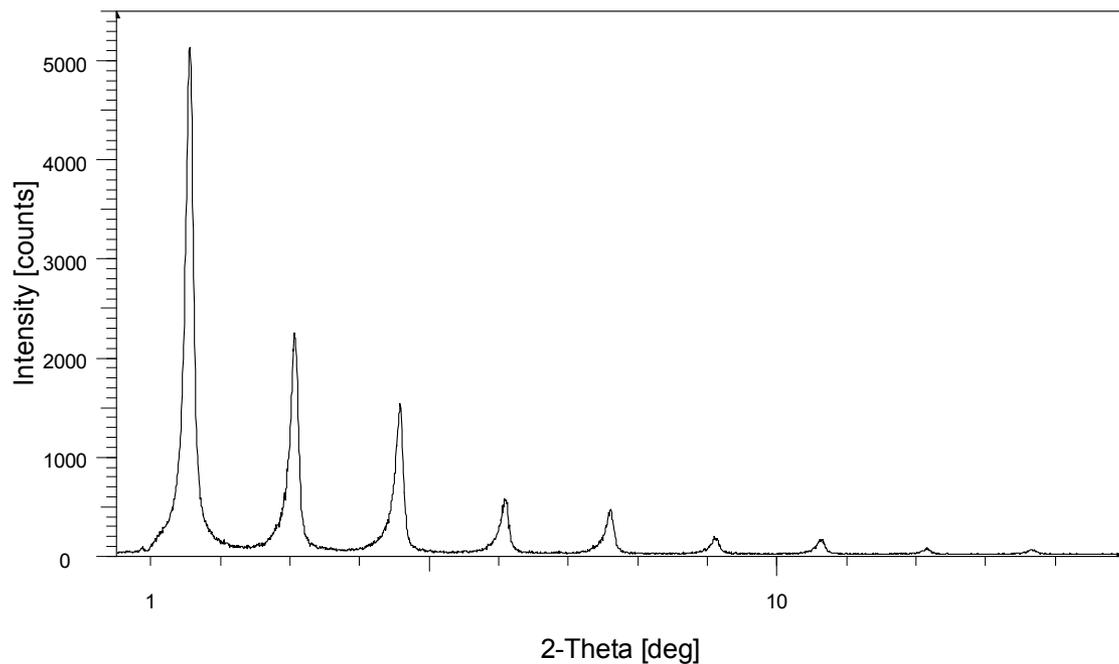


Illustration of a phase change by use of XRPD patterns

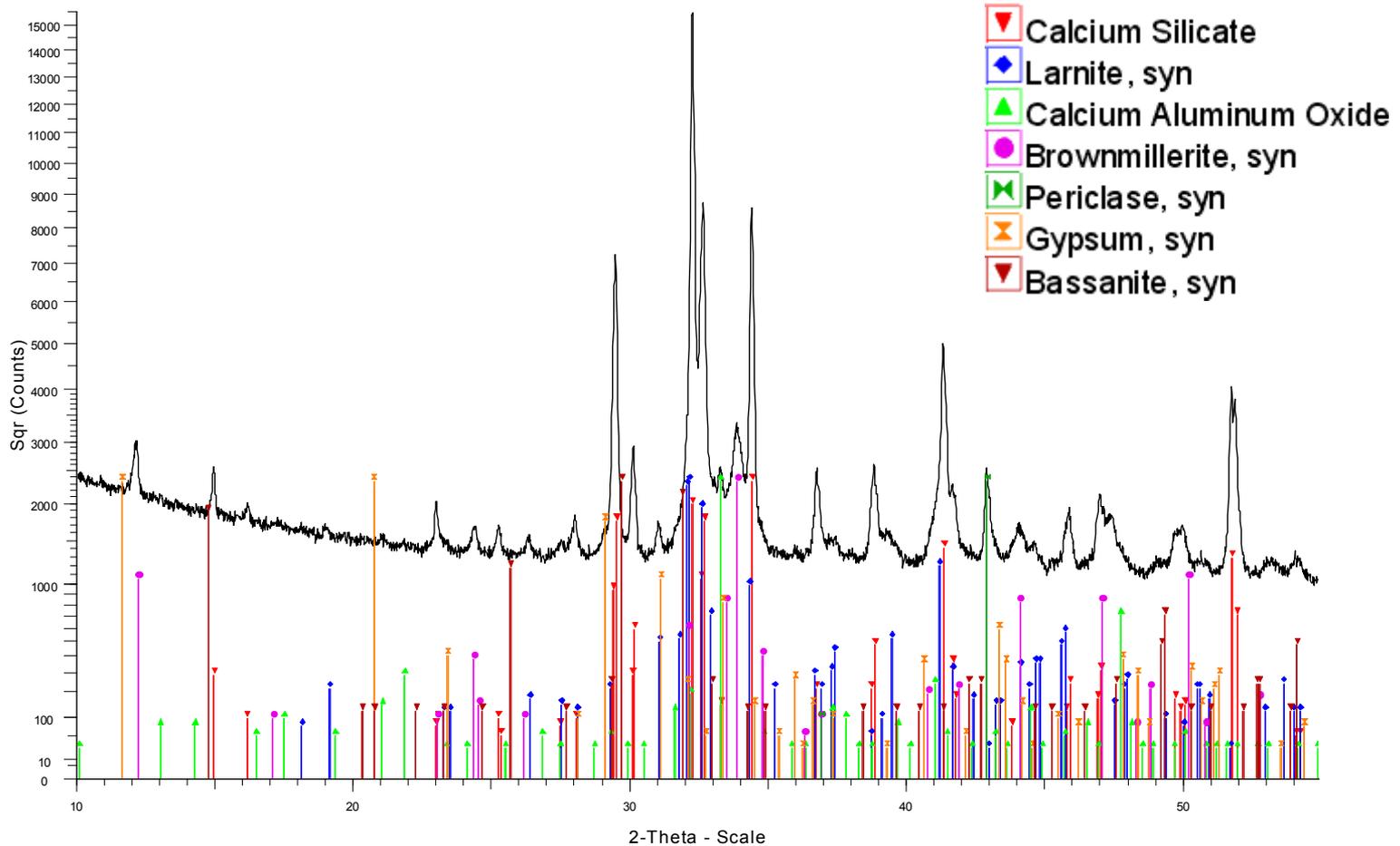
# X-ray Powder Diffraction (XRPD)



- D8 ADVANCE,
- Cu radiation, 40kV/40 mA
- Divergence aperture: 0,1°
- Increment: 0.007°
- Counting time/step: 0.1 sec
- Speed: 4.2°/min.
- Total time: 3:35 min.

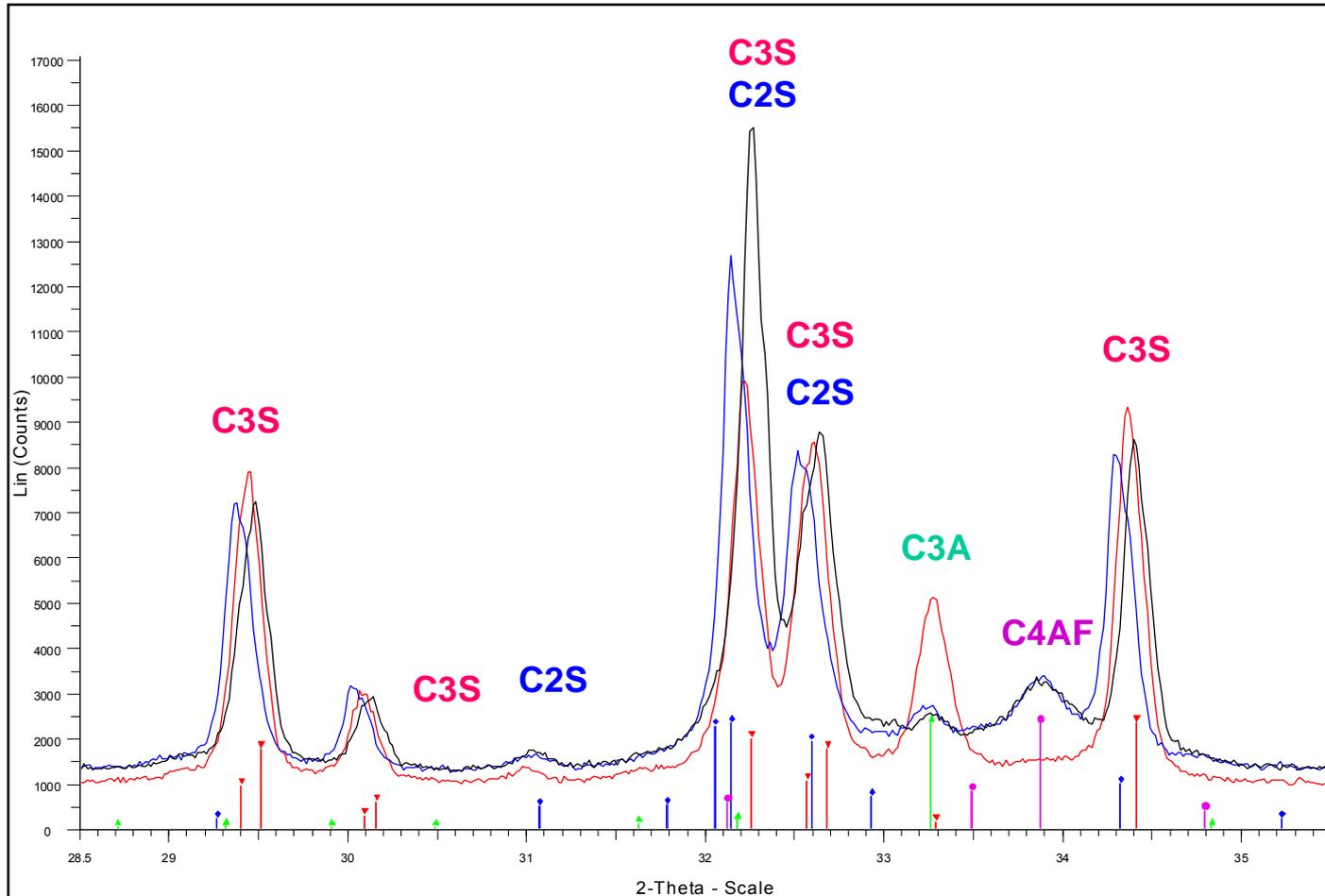
Small angle scattering of silver behenate ( $\text{CH}_3(\text{CH}_2)_{20}\text{-COOAg}$ )  
(Bragg-Brentano geometry)

# X-ray Powder Diffraction (XRPD)



Quantitative phase analysis of cement

# X-ray Powder Diffraction (XRPD)



Quantitative phase analysis of cement

# Literature

- *Röntgenfeinstrukturanalyse* von **H. Krischner**, Vieweg  
(Allgemeine Einführung, Schwerpunkt Pulvermethoden)  
oder alternativ
- *Röntgen-Pulverdiffraktometrie* von **Rudolf Allmann**, Clausthaler  
Tektonische Hefte 29, Sven von Loga, 1994
- *Kristallstrukturbestimmung* von **W. Massa**, Teubner, Stuttgart, 1984
- *Untersuchungsmethoden in der Chemie* von **H. Naumer und W. Heller**,  
Wiley-VCH  
(Einführung in die moderne Analytik und Strukturbestimmungsmethoden)
- *X-Ray Structure Determination* von **G. H. Stout, L.H. Jensen**, MacMillan,  
London  
(Einführung in die Kristallstrukturanalyse für Fortgeschrittene)

