Skript zur Vorlesung Anorganische Chemie I

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(X-ray) Diffraction

Some practical aspects of one of the most important tools in solid state sciences

Bragg's Law of Diffraction

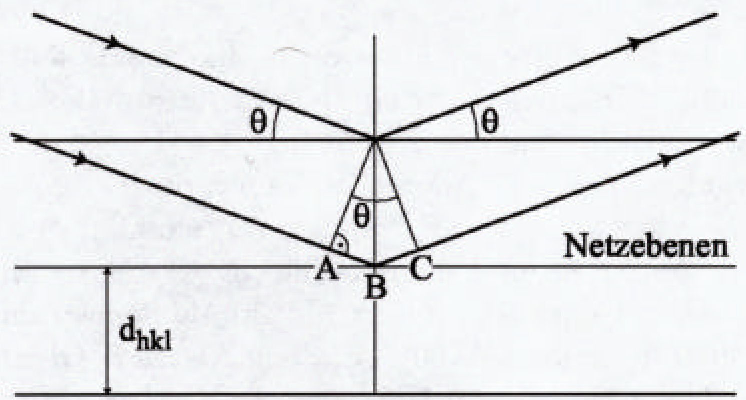


Abbildung 28: Beugung von Röntgenstrahlung an einem Kristall (siehe Text).

constructive interference only, when:

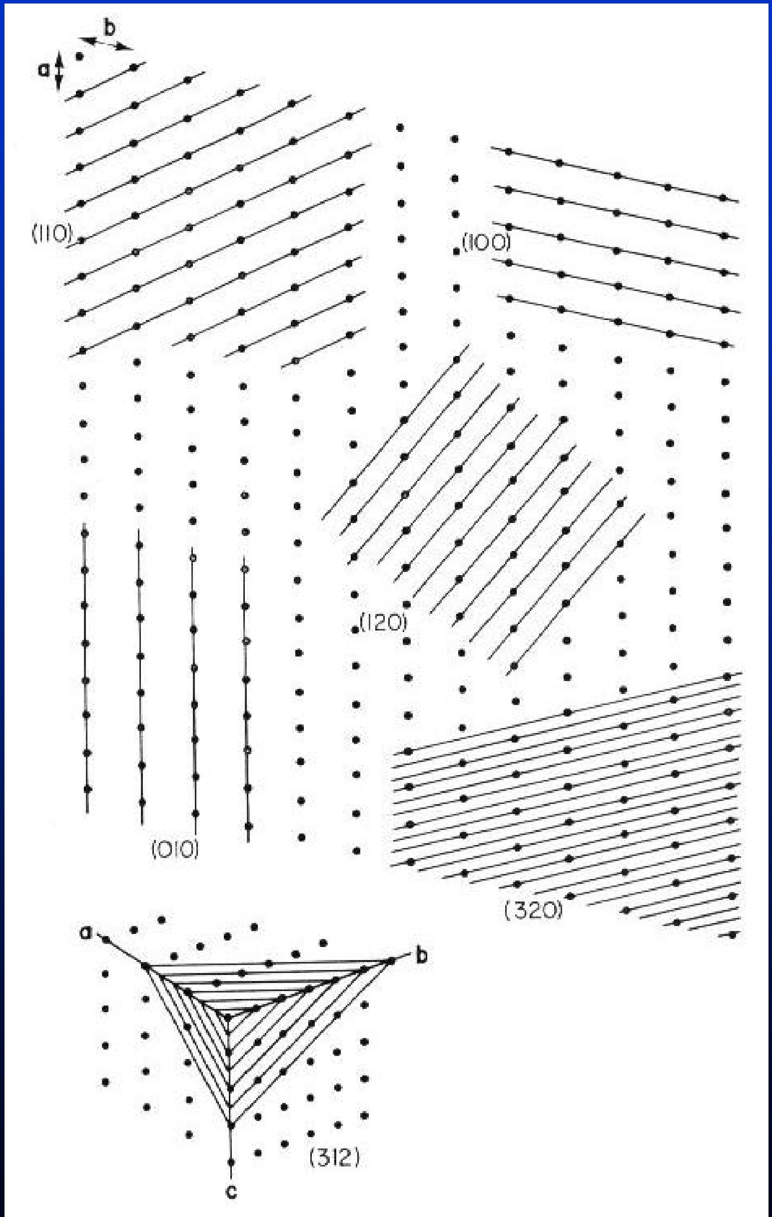
$\Delta = n \cdot \lambda$ ($\Delta = AB + BC$)

with:

$\sin\theta = (\Delta/2)/d$

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

Diffraction from Lattice Planes

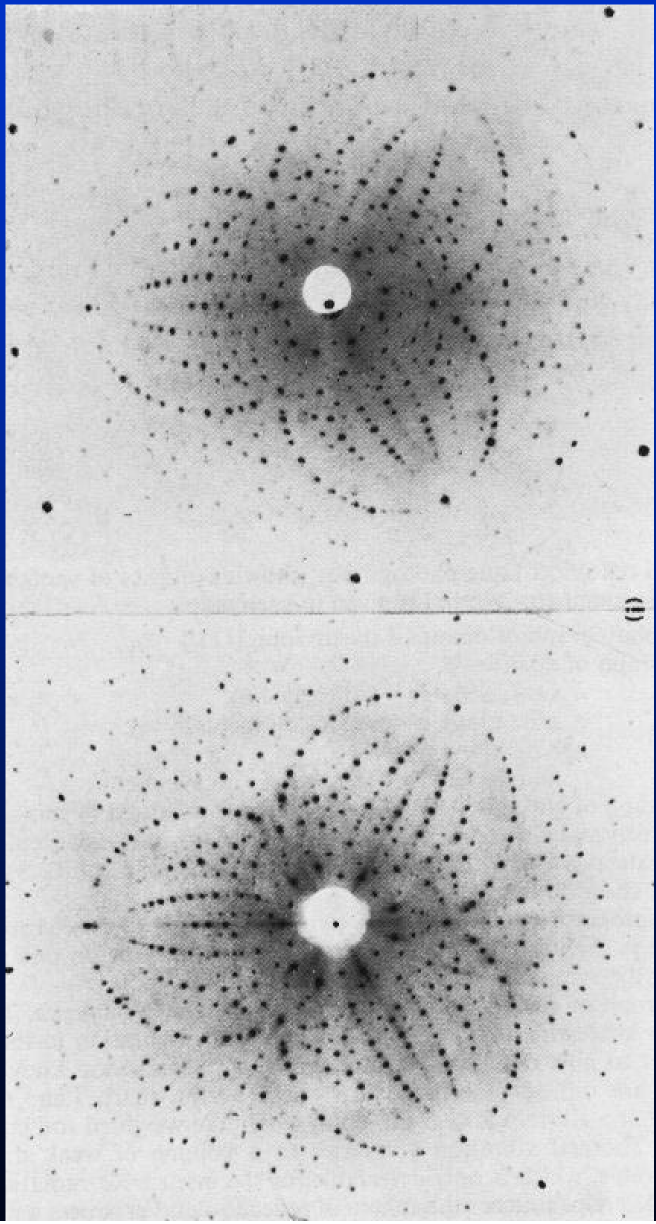


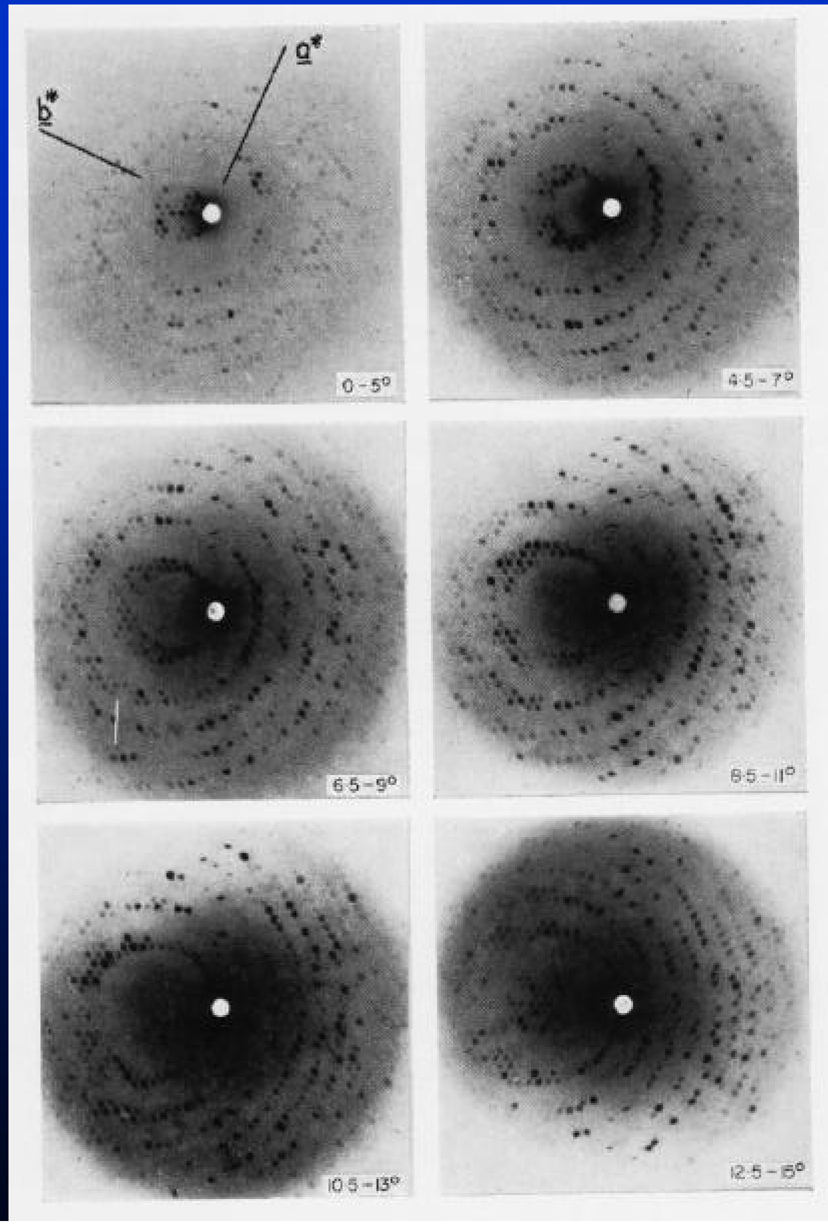
•Each set of planes corresponds to

one structure factor

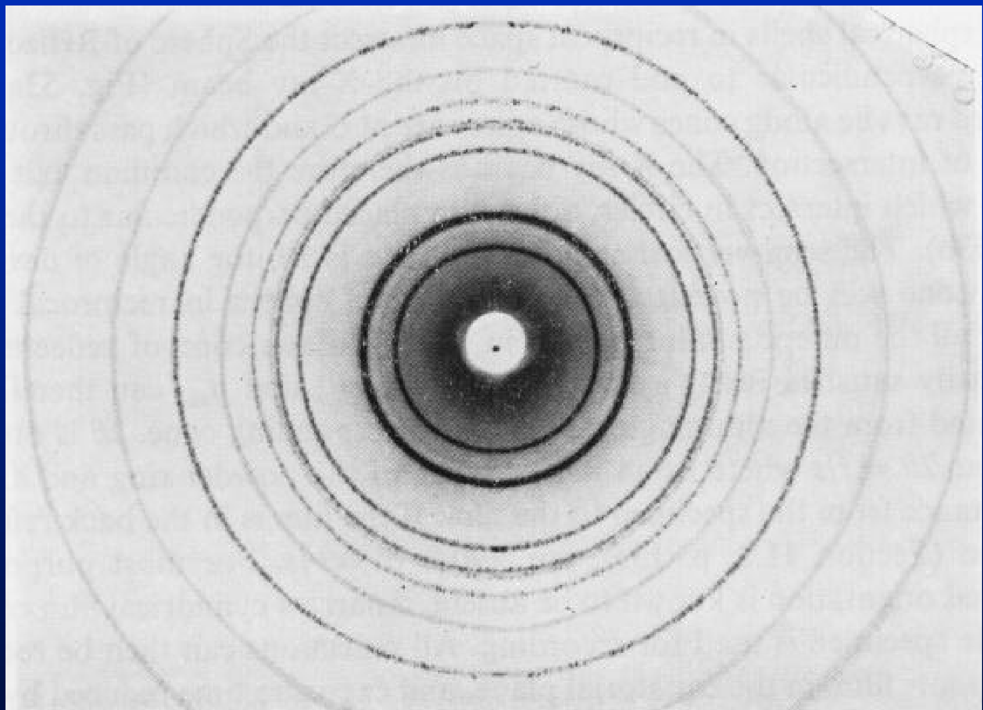
S_{hkl}

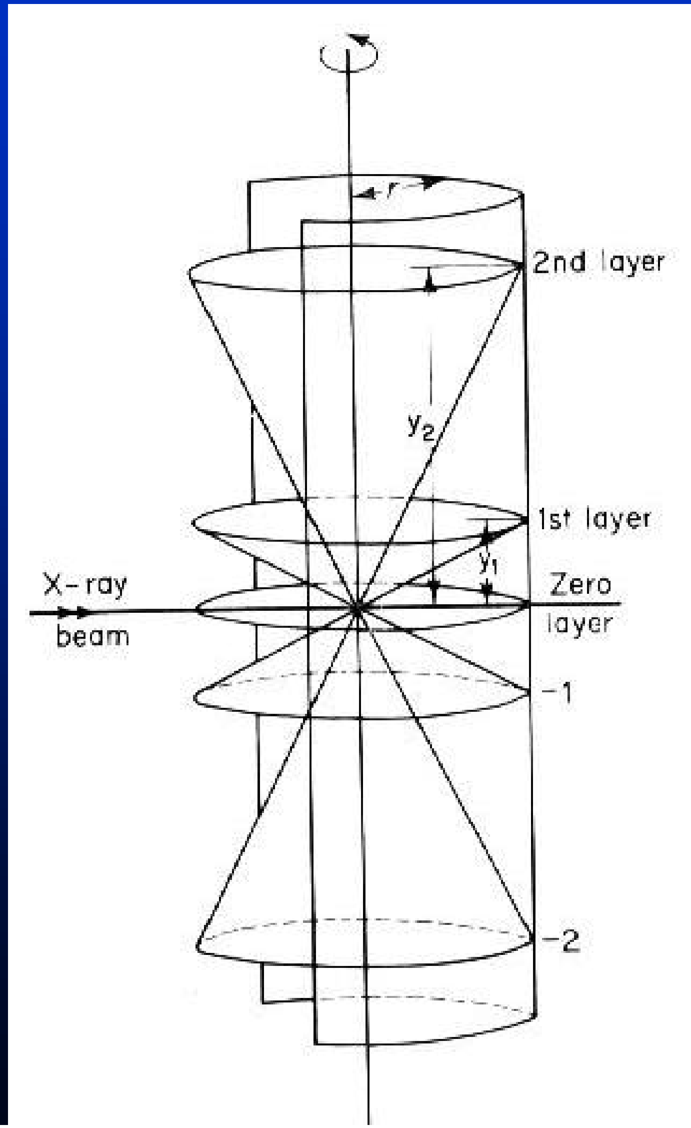
Diffraction from Single Crystals





Diffraction from Powder Crystals





Quadratic Bragg formulas

Tabelle 4: Die quadratischen Braggschen Gleichungen in den 7 Kristallsystemen

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Triklin

$$\sin^2\theta = \frac{\lambda^2}{4}[h^2a^{*2} + k^2b^{*2} + l^2c^{*2} + 2klb^*c^*\cos\alpha^* + 2lhc^*a^*\cos\beta^* + 2hka^*b^*\cos\gamma^*]$$

$$a^* = \frac{1}{V}bc\sin\alpha, \qquad \cos\alpha^* = \frac{\cos\beta\cos\gamma - \cos\alpha}{\sin\beta\sin\gamma}$$

$$b^* = \frac{1}{V}ca\sin\beta, \qquad \cos\beta^* = \frac{\cos\gamma\cos\alpha - \cos\beta}{\sin\gamma\sin\alpha}$$

$$c^* = \frac{1}{V}ab\sin\gamma, \qquad \cos\gamma^* = \frac{\cos\alpha\cos\beta - \cos\gamma}{\sin\alpha\sin\beta}$$

$$V = abc\sqrt{1 + 2\cos\alpha\cos\beta\cos\gamma - \cos^2\alpha - \cos^2\beta - \cos^2\gamma}$$

Monoklin

$$\sin^2\theta = \frac{\lambda^2}{4}\left[\frac{h^2}{a^2\sin^2\beta} + \frac{k^2}{b^2} + \frac{l^2}{c^2\sin^2\beta} - \frac{2hl\cos\beta}{ac\sin^2\beta}\right]$$

Orthorhombisch

$$\sin^2\theta = \frac{\lambda^2}{4}\left[\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}\right]$$

Tetragonal

$$\sin^2\theta = \frac{\lambda^2}{4a^2}\left[h^2 + k^2 + \left(\frac{a}{c}\right)^2 l^2\right]$$

Hexagonal und trigonal

$$\sin^2\theta = \frac{\lambda^2}{4a^2}\left[\frac{4}{3}(h^2 + k^2 + hk) + \left(\frac{a}{c}\right)^2 l^2\right]$$

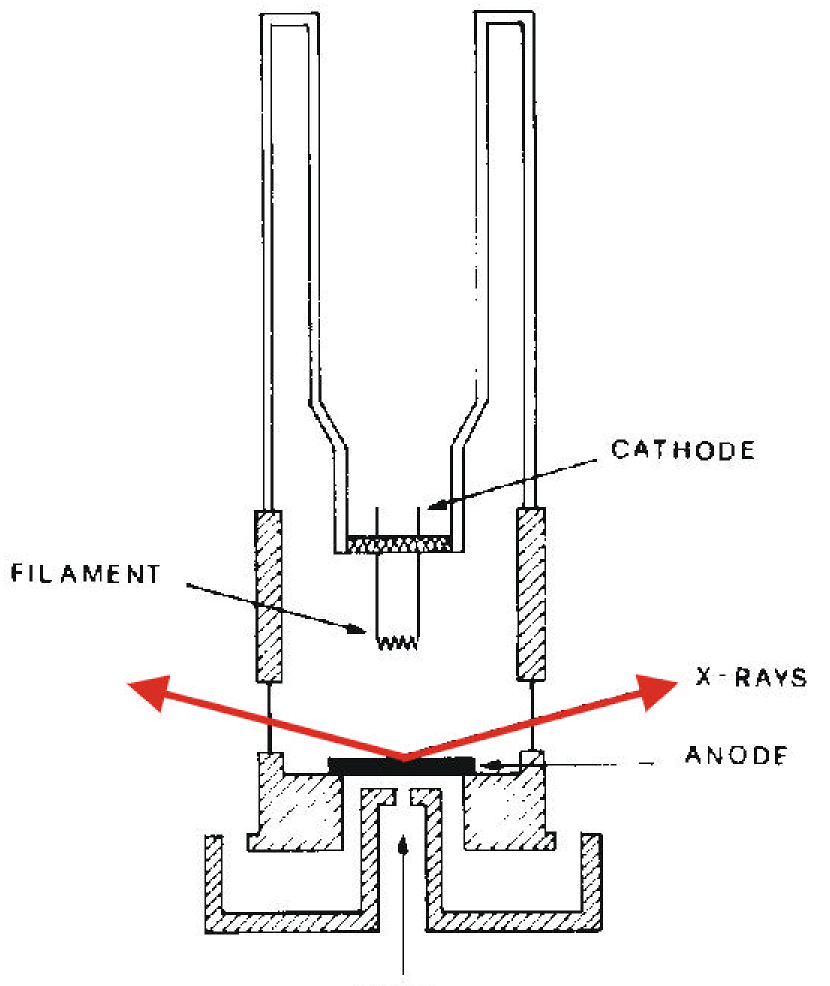
Kubisch

$$\sin^2\theta = \frac{\lambda^2}{4a^2}[h^2 + k^2 + l^2]$$

Working Principle of the X-ray tube

- Tungsten wire at 1200-1800ºC (about 35mA heating current)
- High Voltage 20-60 kV
- max. Power 2.2-3 kW

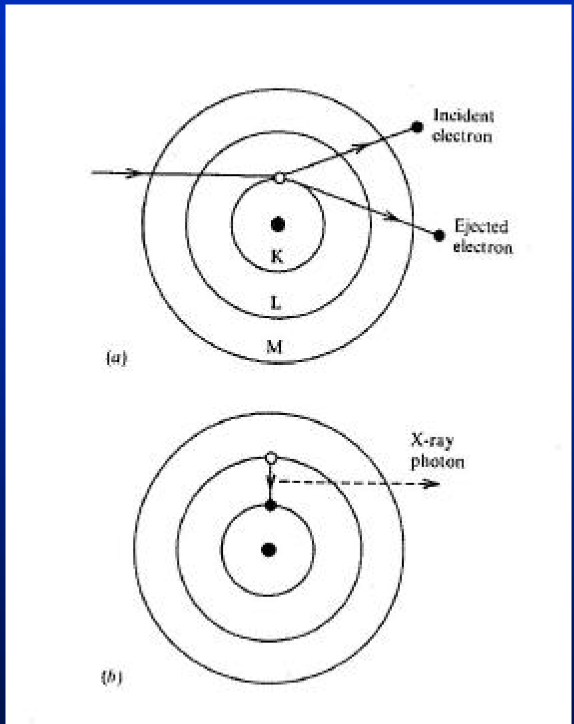
•Typical operating values for
Cu: 40 kV, 35 mA
Mo: 45 kV, 35 mA



(a)

Spectrum of the X-ray tube

Characteristic radiation



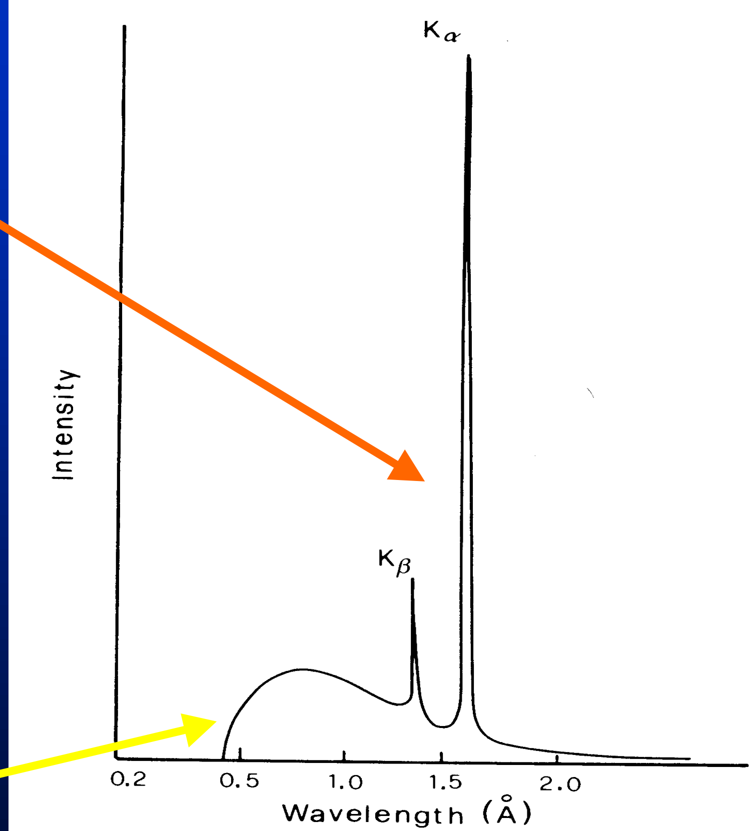


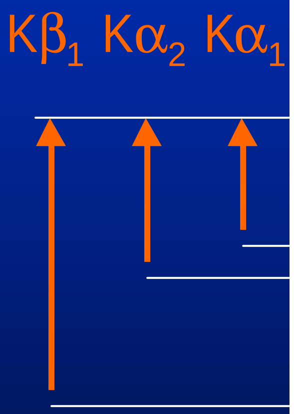
Fig. 4.2. Characteristic spectrum of copper superimposed on the white radiation spectrum. Notice the ratio of the relative intensities of the K_α and K_β lines.

Bremstrahlung (white radiation)

$E_{max.} = E_0 = e \cdot V_0$ and with $E = (h \cdot c)/\lambda$:

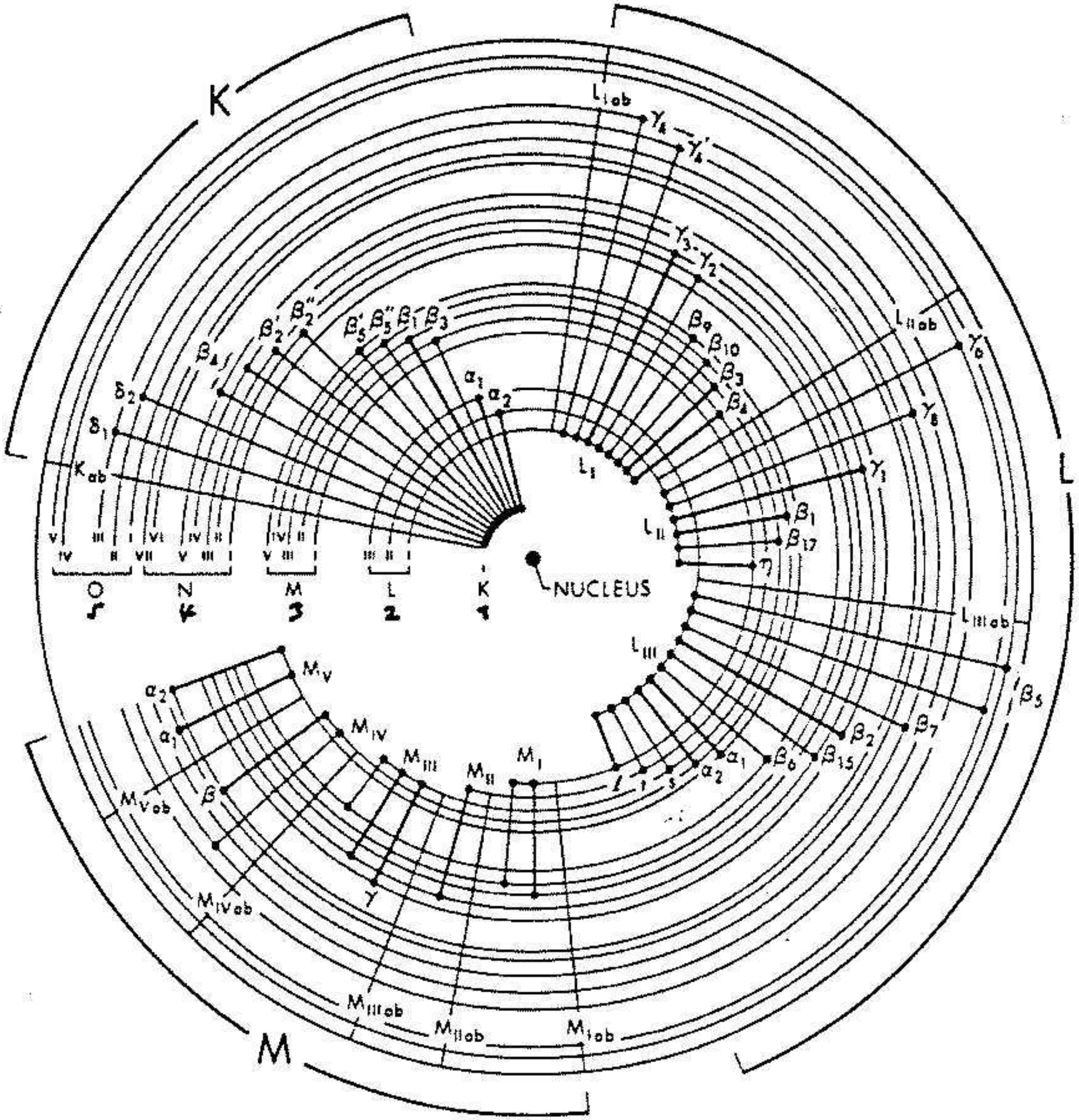
$\lambda_{min}/\text{Å} = (h \cdot c)/e \cdot V_0 = 12.34/(V_0/\text{kV})$

- n=1,2,3 (principal quantum number), corresponds to K, L, M... shells
- l=0, 1, ..., n-1 (orbital quantum number)
- j=|l⊕s|; s=1/2 (spin-orbit coupling)
- m_j=j, j-1, j-2, ..., -j
- Rules: Transition only, when Δl🕒0



X-ray notation	Quantum numbers				Maximum electron population
	n	l	j	m_j	
K	1	0	$\frac{1}{2}$	$\pm\frac{1}{2}$	2
L_I	2	0	$\frac{1}{2}$	$\pm\frac{1}{2}$	2
L_{II}	2	1	$\frac{1}{2}$	$\pm\frac{1}{2}$	2
L_{III}	2	1	$\frac{3}{2}$	$\pm\frac{3}{2}, \pm\frac{1}{2}$	4
M_I	3	0	$\frac{1}{2}$	$\pm\frac{1}{2}$	2
M_{II}	3	1	$\frac{1}{2}$	$\pm\frac{1}{2}$	2
M_{III}	3	1	$\frac{3}{2}$	$\pm\frac{3}{2}, \pm\frac{1}{2}$	4
M_{IV}	3	2	$\frac{3}{2}$	$\pm\frac{3}{2}, \pm\frac{1}{2}$	4
M_V	3	2	$\frac{5}{2}$	$\pm\frac{5}{2}, \pm\frac{3}{2}, \pm\frac{1}{2}$	6
N_I	4	0	$\frac{1}{2}$	$\pm\frac{1}{2}$	2
N_{II}	4	1	$\frac{1}{2}$	$\pm\frac{1}{2}$	2
N_{III}	4	1	$\frac{3}{2}$	$\pm\frac{3}{2}, \pm\frac{1}{2}$	4
N_{IV}	4	2	$\frac{3}{2}$	$\pm\frac{3}{2}, \pm\frac{1}{2}$	4
N_V	4	2	$\frac{5}{2}$	$\pm\frac{5}{2}, \pm\frac{3}{2}, \pm\frac{1}{2}$	6
N_{VI}	4	3	$\frac{5}{2}$	$\pm\frac{5}{2}, \pm\frac{3}{2}, \pm\frac{1}{2}$	6
N_{VII}	4	3	$\frac{7}{2}$	$\pm\frac{7}{2}, \pm\frac{5}{2}, \pm\frac{3}{2}, \pm\frac{1}{2}$	8

• Allowed Transitions



Mosley's Law (for multiple electron atoms):

$$1/\lambda = c \cdot (Z-\sigma)^2 \cdot (1/n_1^2 - 1/n_2^2)$$

- Z = atom number
- σ = shielding constant
- n = quantum number

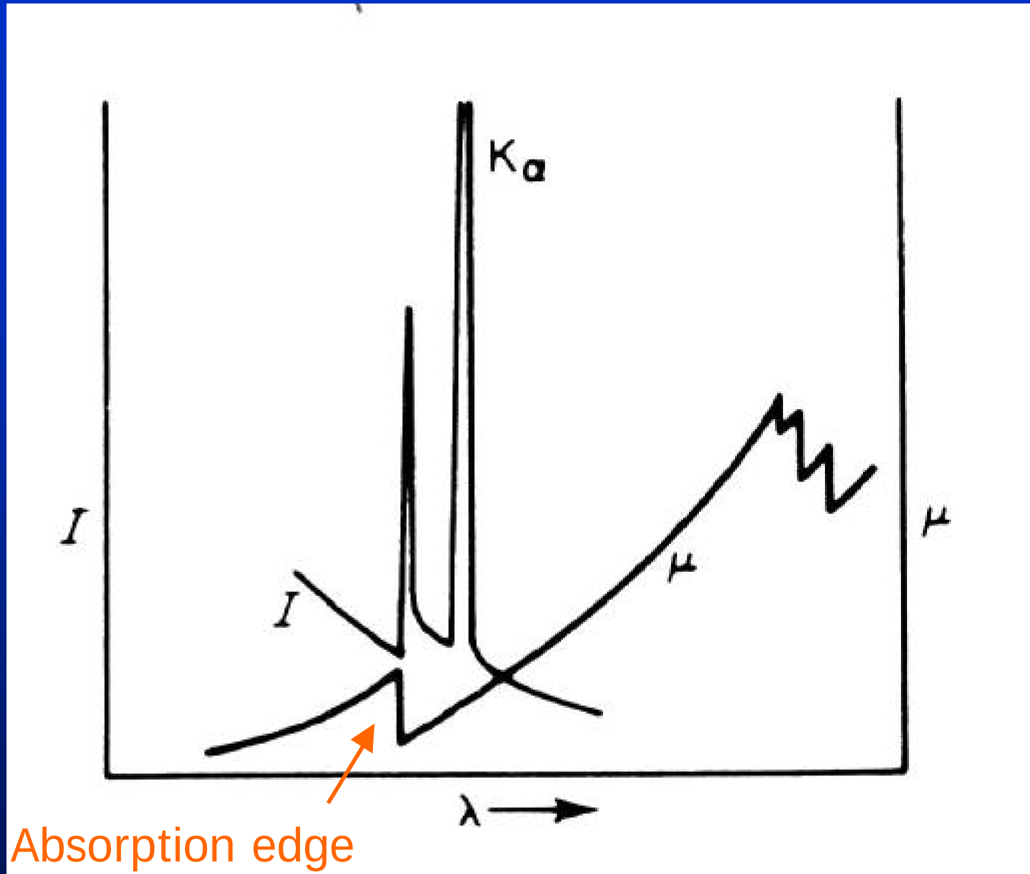
$\Rightarrow$ Decreasing wavelength with increasing Z

Characteristic Wavelengths

in Angstroems (100pm)

Element Symbol	$K\alpha_2$	$K\alpha_1$	$K\beta$	K abs. edge
Cu	1.54433	1.54051	1.39217, 1.38102	1.380
Mo	0.713543	0.70926	0.62099	0.61977
Ag	0.563775	0.559363	0.49701, 0.48701	0.4858
W	0.213813	0.208992	0.17950	0.17837

μ vs. λ



At the absorption edge, the incident X-ray quantum is energetic enough to knock an electron out of the orbital

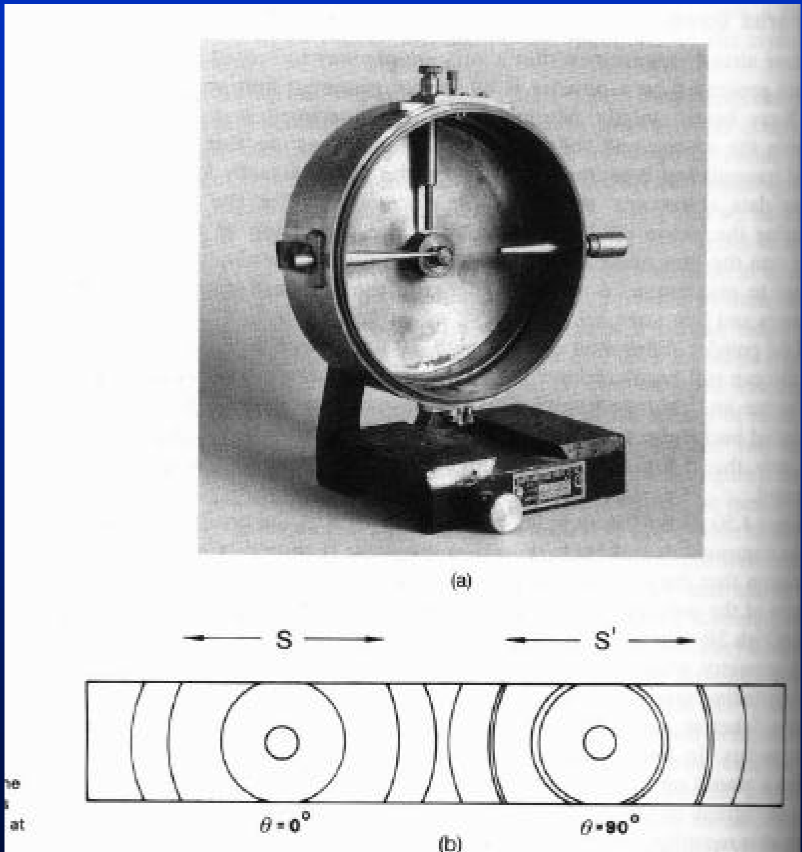
Monochromatisation of X-rays

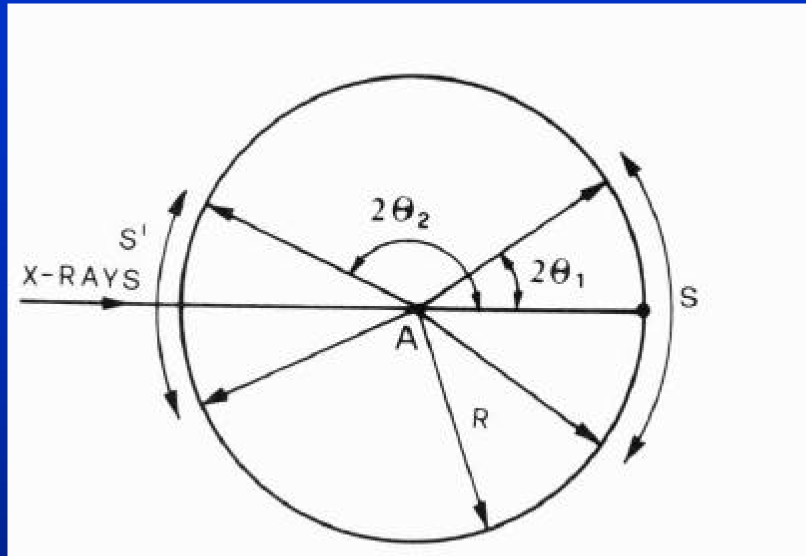
- Filters
- Crystal Monochromators

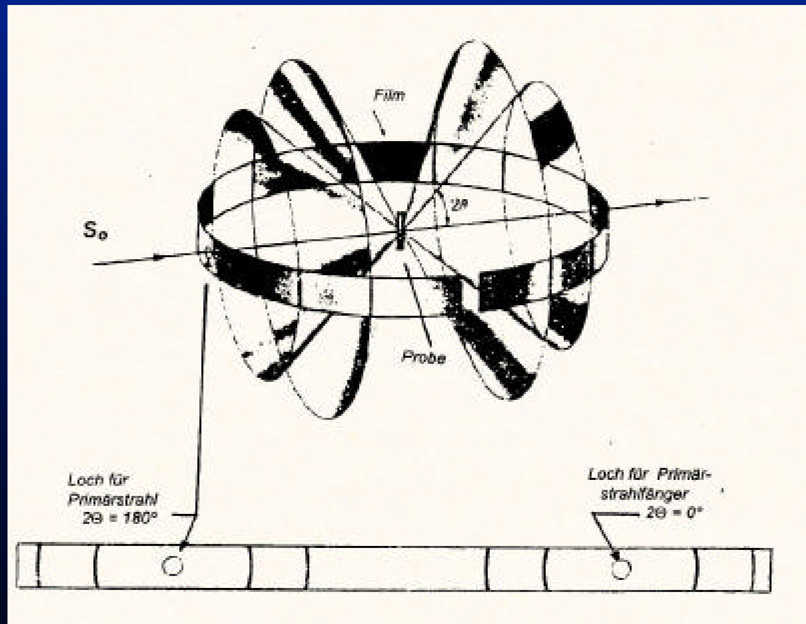
Different Geometries

- Debye-Scherrer
- Bragg-Brentano
- Guinier

Debye Scherrer



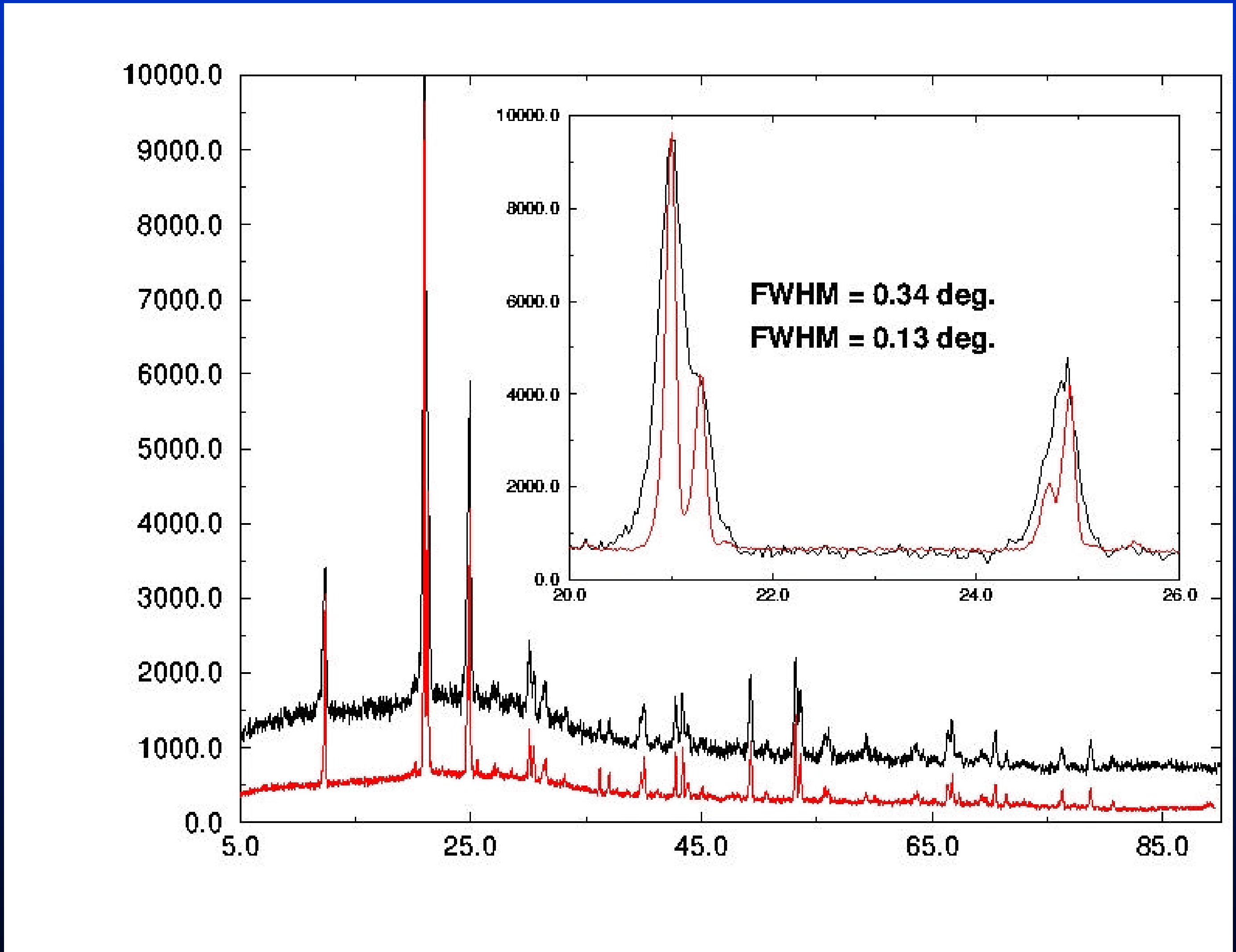




Detection of X-rays

- Film (Guinier camera, Debye-Scherrer Camera, precession camera)
- Si(Li) solid state detector (powder diffractometers)
- Szintillation counter (4-circle diffractometer,Stoe powder diffractometer)
- Position Sensitive Detectors (Stoe powder diffractometer)
- Image Plate Detectors(Stoe IPDS)
- CCD Detectors (Bruker SMART system)

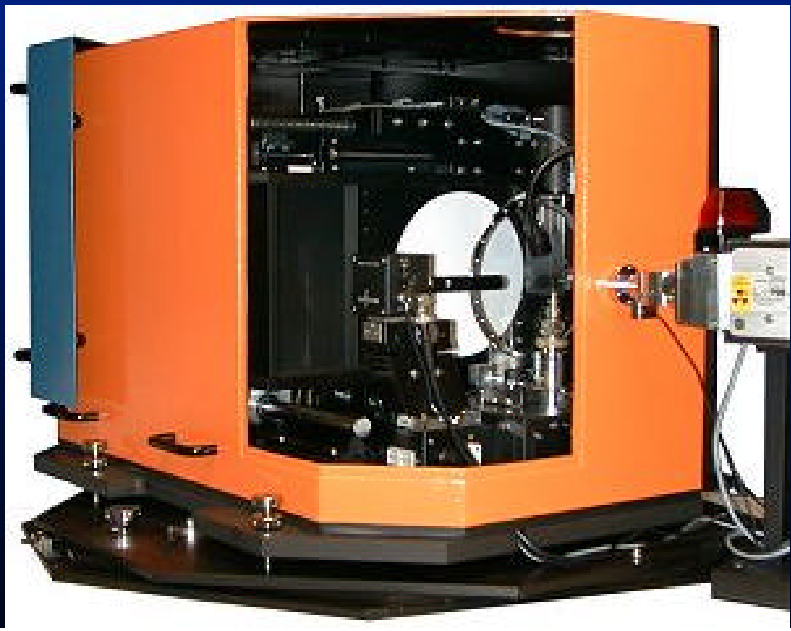
Resolution:



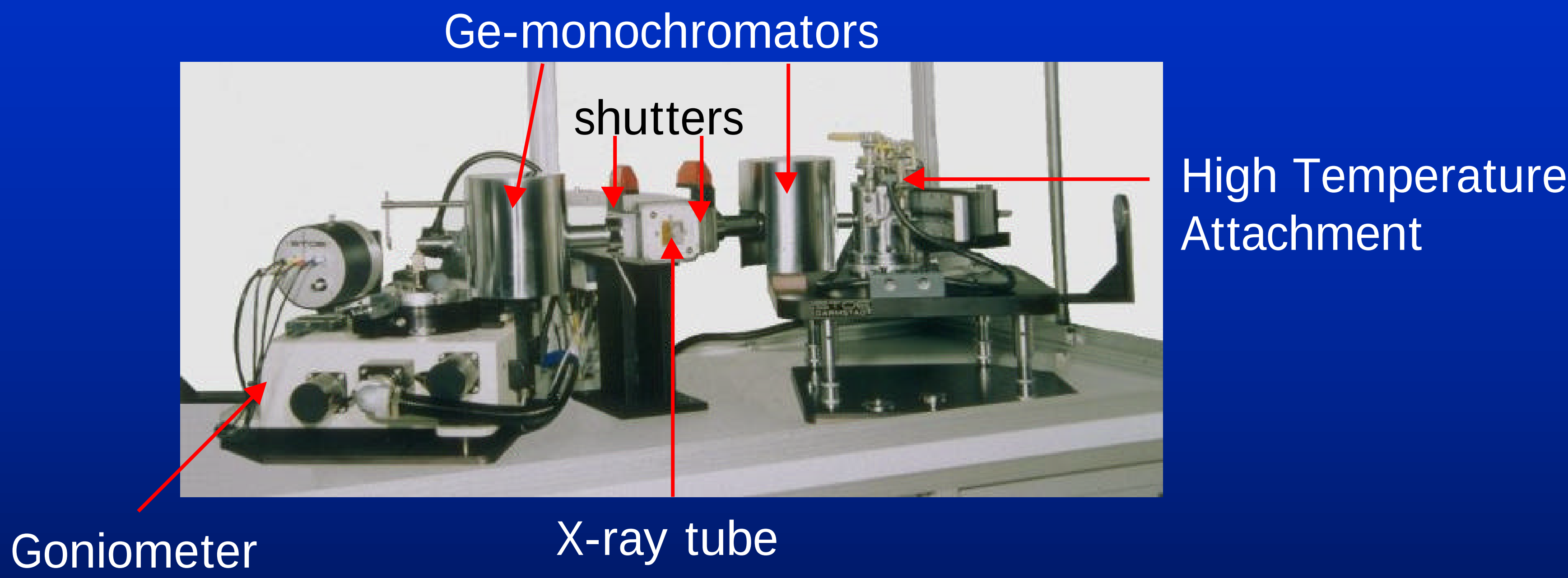
10000.0
9000.0
8000.0
7000.0
6000.0
5000.0
4000.0
3000.0
2000.0
1000.0
0.0
5.0
25.0
45.0
65.0
85.0
10000.0
8000.0
6000.0
4000.0
2000.0
0.0
20.0
22.0
24.0
26.0
FWHM = 0.34 deg.
FWHM = 0.13 deg.

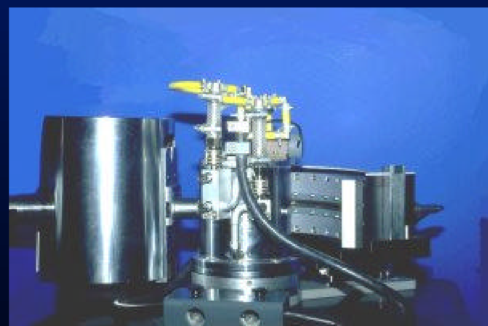
Image plate detectors

- Metal plate with about 18cm diameter, coated with Eu^{2+} doped BaFBr
- X-rays ionize Eu^{2+} to Eu^{3+} and the electrons are trapped in color centers
- Read out process with red laser leads to emission of blue light, when electrons return to ground state
- The blue light is amplified by a photomultiplier and recorded as a pixel image

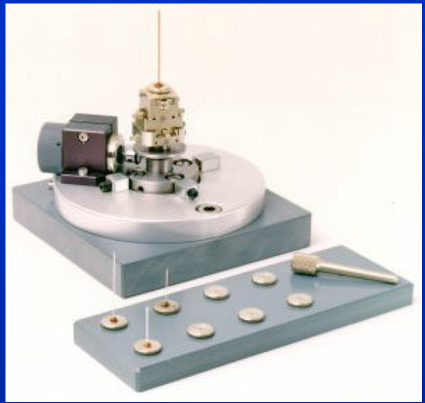


Setup for a Powder Diffractometer





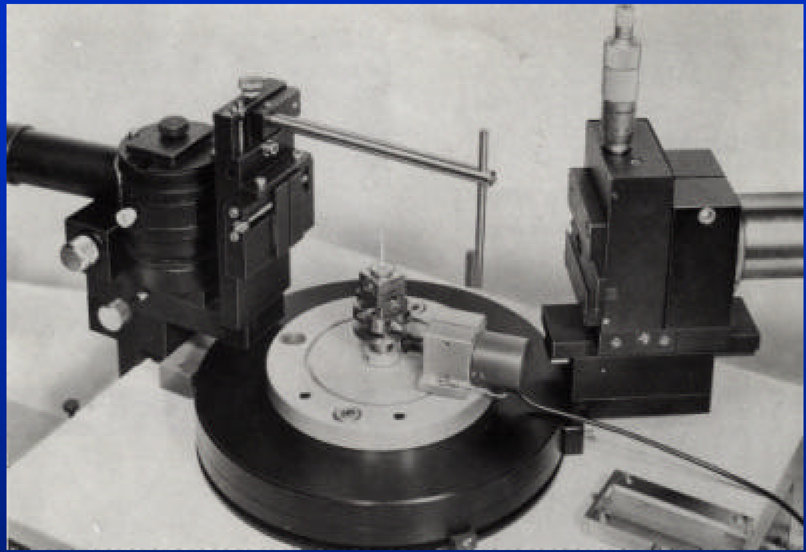
Different Sample Holders

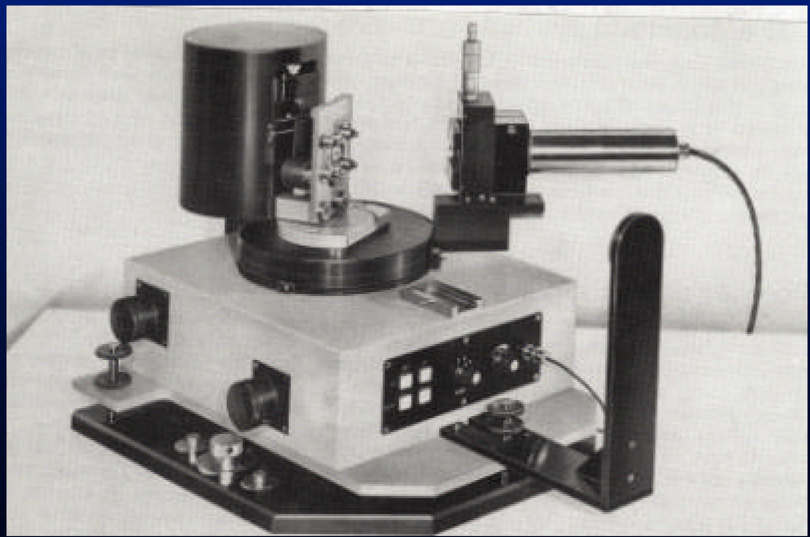


Capillary

Transmission

Reflection





Preparing a sample

Capillary:

For air sensitive samples

Diameter between 0.1 an 1mm, Standard is 0.3 mm

For samples with high absorption 0.1 mm is better suited

Difficulties with soft samples which are not easy to fill in

Transmission sample holder

Good for samples which are not or only moderately air sensitive.

Sample is placed on a Scotch (Tesa) strip and covered with a second strip.

Be sure, that the sample is only on one(!) side and the second is only for protection.

Reflection sample holder

Only for moderately air sensitive samples

Good for or strongly absorbing samples like for example electrodes or thin films on a substrate

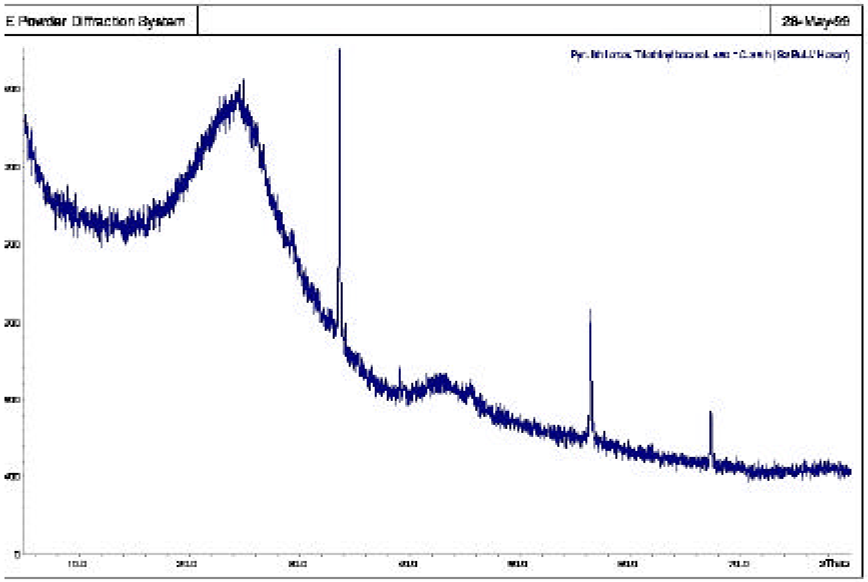
Is used at the moment for in situ electrochemical cell experiments

Cannot be used in connection with the large PSD

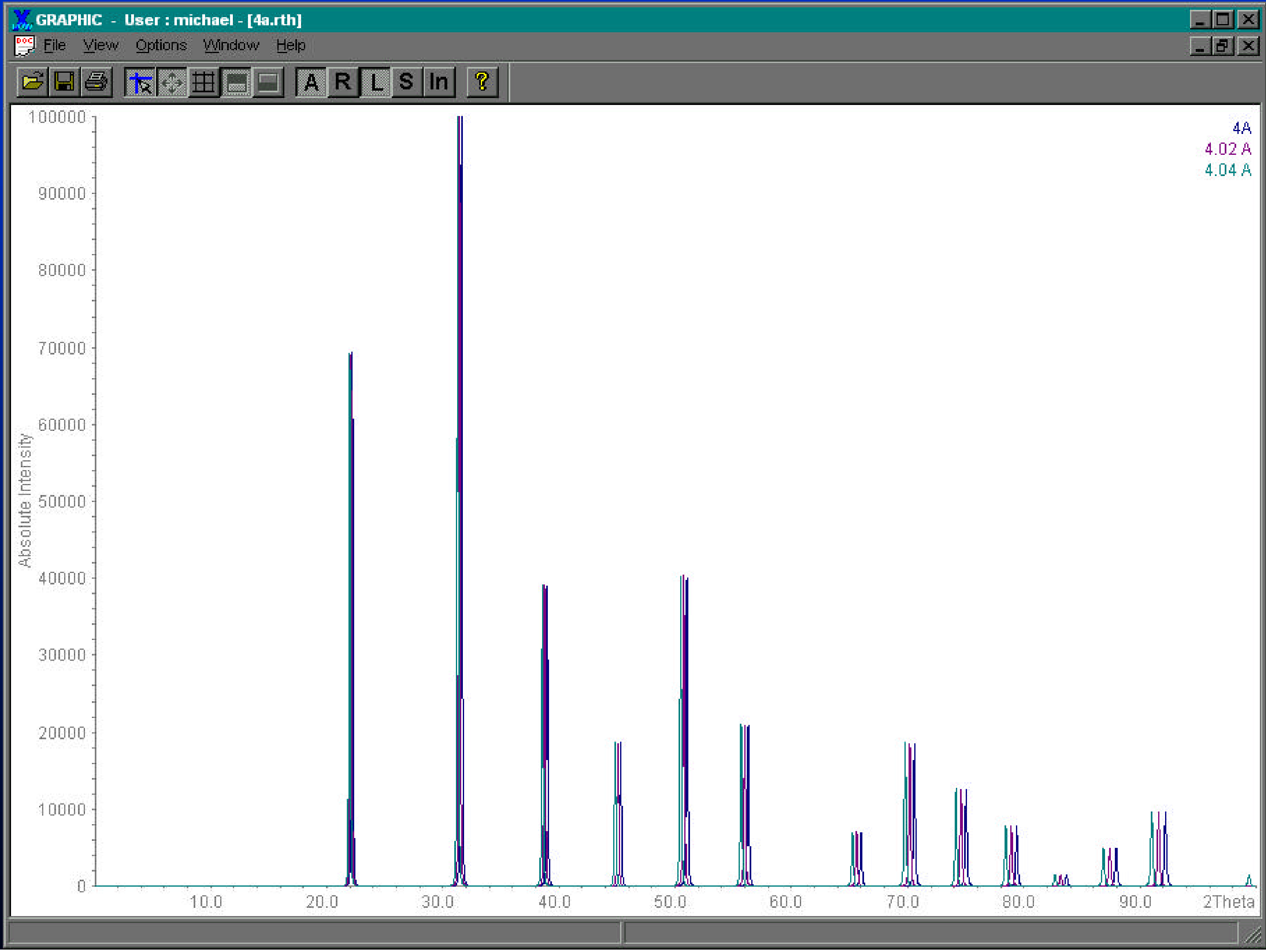
What Information Can We Extract from Diffraction Experiments?

- Determination of known phases
- Crystallinity
- Determination of lattice constants
- Structure solution

Crystalline and Amorphous Phase together:



Effect of a Change of the Lattice Constants

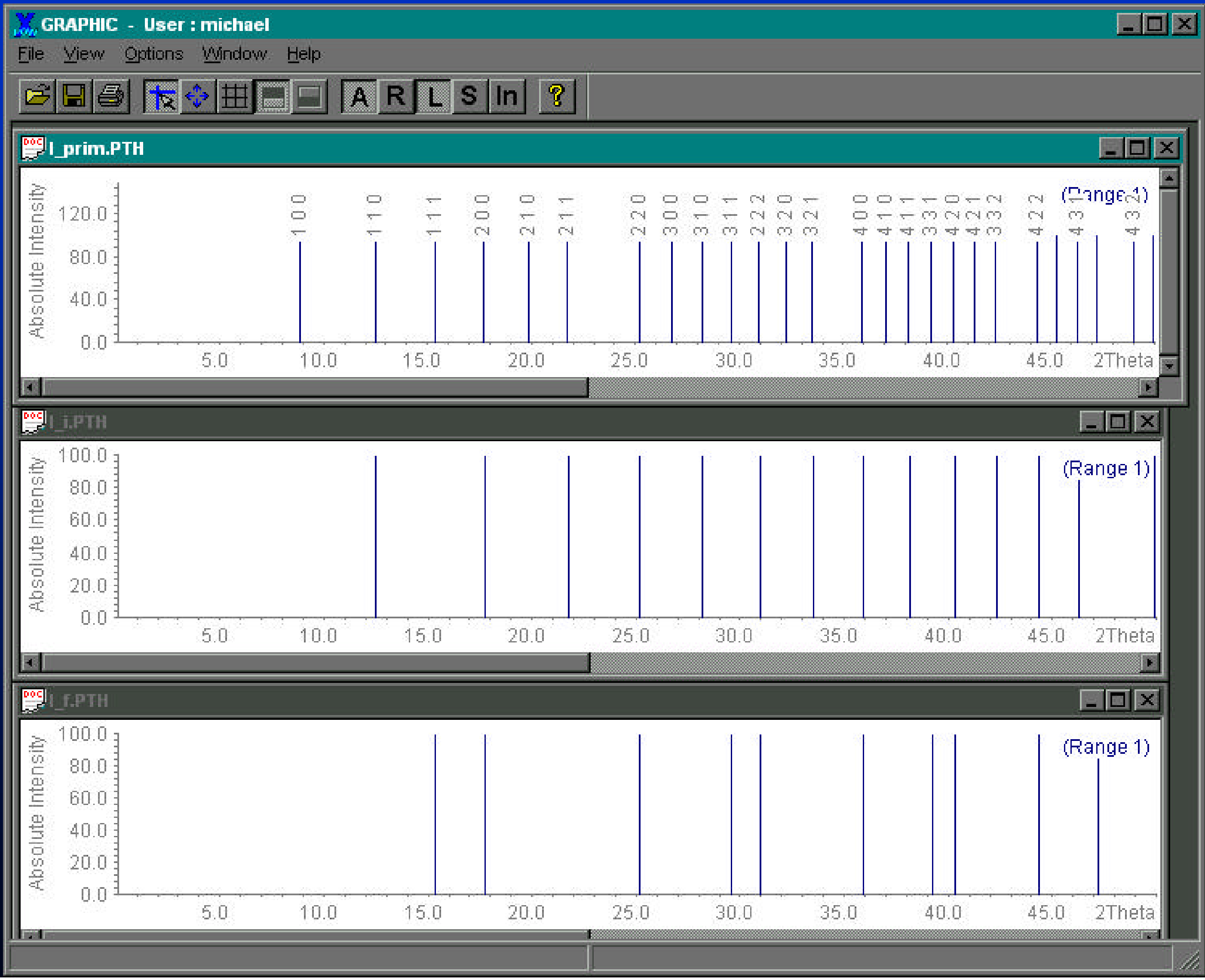


Effect of Centering

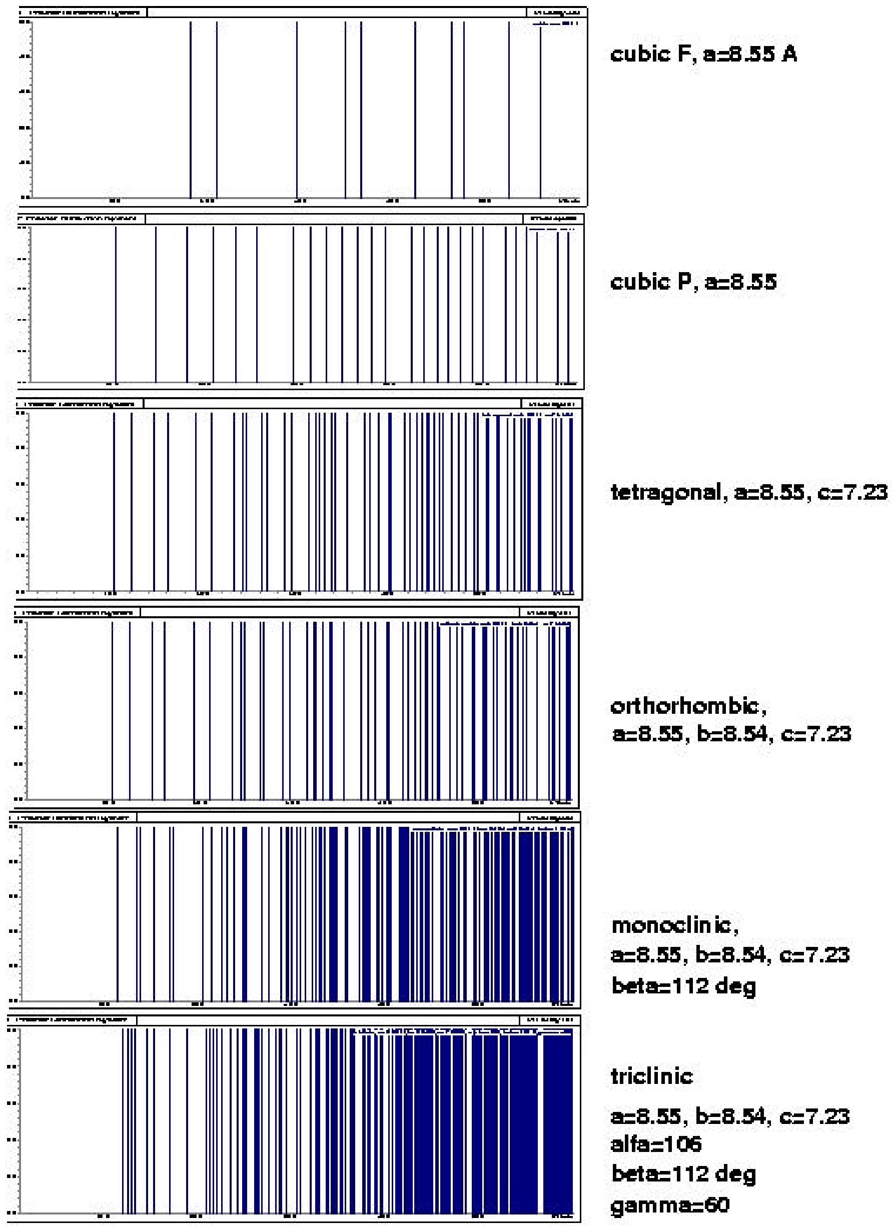
P

I

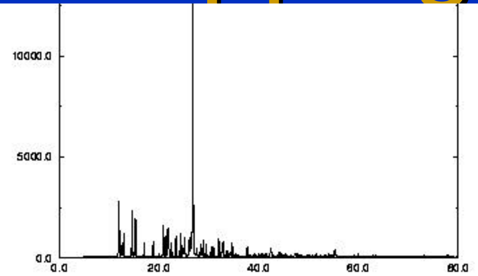
F



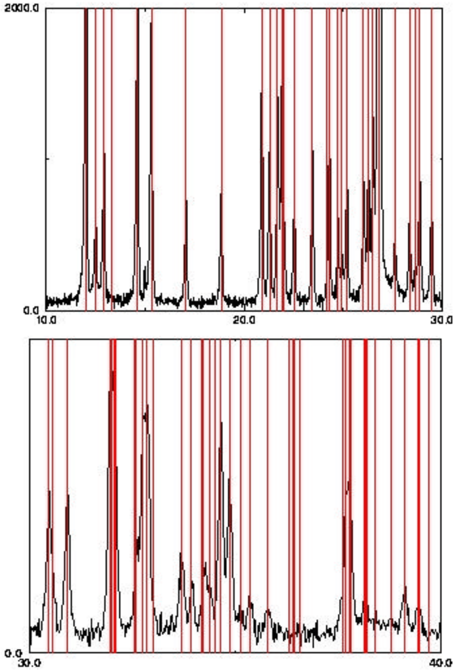
Number of lines changes with symmetry

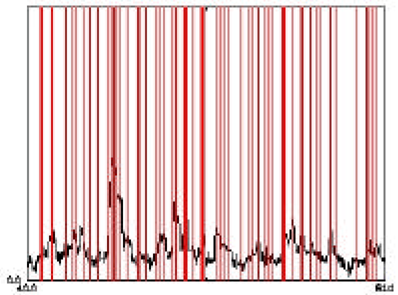


Overlapping of Reflections:



triclinic a=8.55, b=8.54, c=7.23 alfa=106 beta=112 deg gamma=60





Databases:

- ICSD (Inorganics, Single Crystal Data, on PC's)
- CSD (Organics, on Wawona)
- METALS (at vsibm1.mpi-stuttgart.mpg.de, username guest, password guest, metals)

Interaction of Electrons with Matter

Emission of electromagnetic radiation:

- Characteristic radiation, discrete energies, $E_C < E_0$
- Bremsstrahlung, continuous energie distribution, $E_b \leq E_0$
- Luminescence, in the UV or visible Region

Electron emission:

- Backscattered electrons (BSE)
- Auger electrons
- Secondary electron emission (SE)

Effects in the Target:

- Electron Absorption (ABS)
- Heat