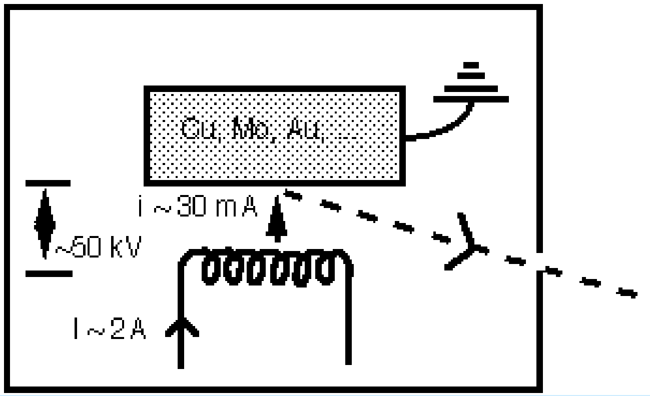
X-rays

Wilhelm K. Roentgen
(1845-1923)
NP in Physics 1901

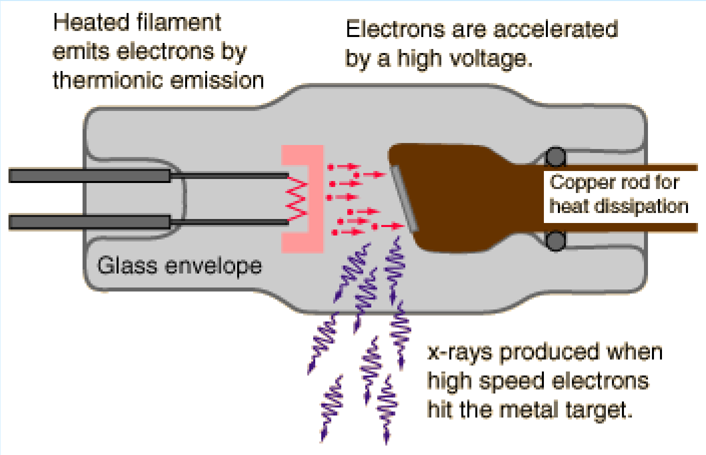
- X-ray Radiography - absorption is a function of Z and density

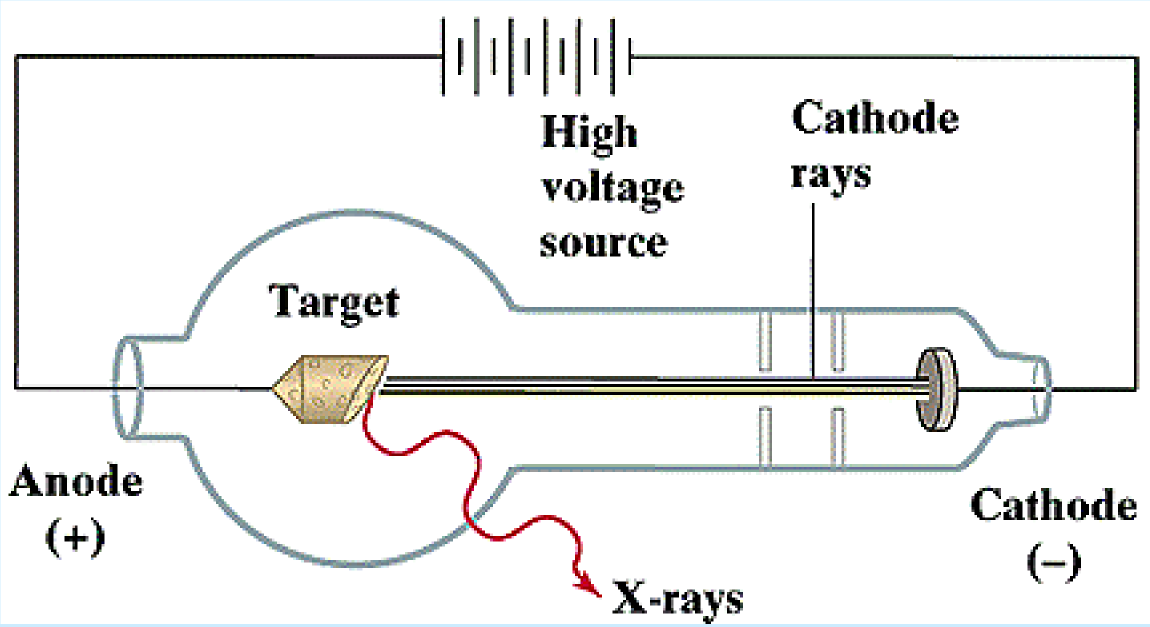
- X-ray crystallography

- X-ray spectrometry



X-rays





Cu K_α $E = 8.05$ keV $\lambda = 1.541$ Å

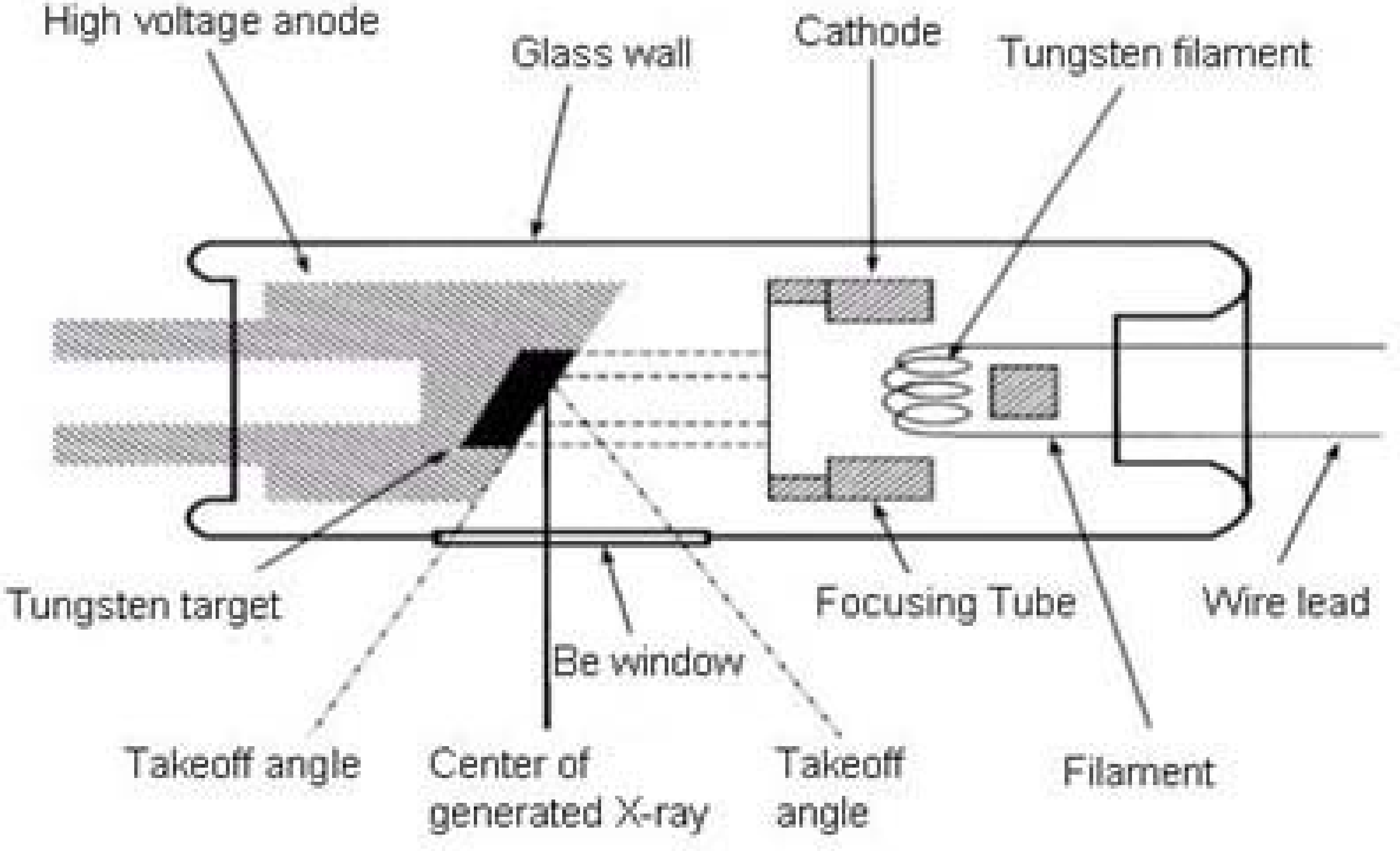
Interaction of Electrons with Matter

Emission of electromagnetic radiation:
- Characteristic radiation, discrete energies
- Bremsstrahlung, continuous energy distribution
- Luminiscence (UV or visible region)

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

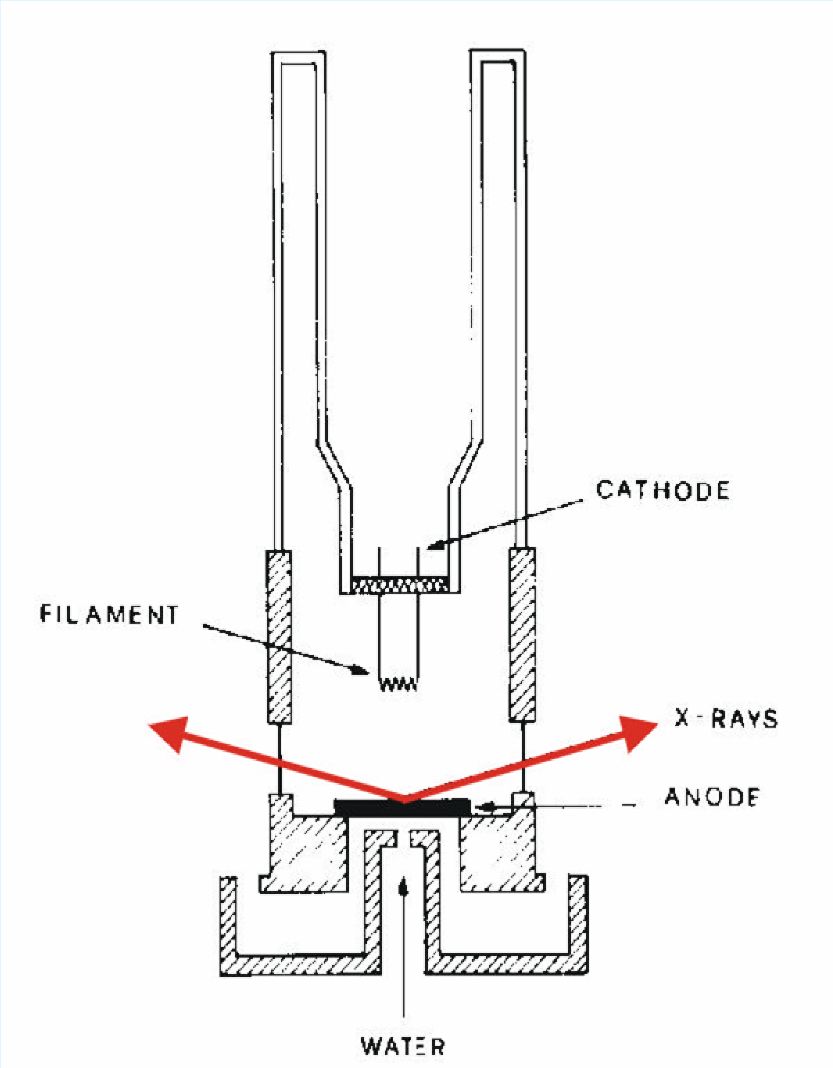
Effects in the Target:
- Electron Absorption (ABS)
- Heat

X-ray Tubes



X-ray tube

X-ray Tubes



Tungsten wire at 1200-1800 °C
(about 35 mA heating current)

High Voltage 20-60 kV High

max. power 2.2-3 kW

Typical operating values

Cu: 40 kV, 35 mA

Mo: 45 kV, 35 mA

Spectrum of the X-ray tube

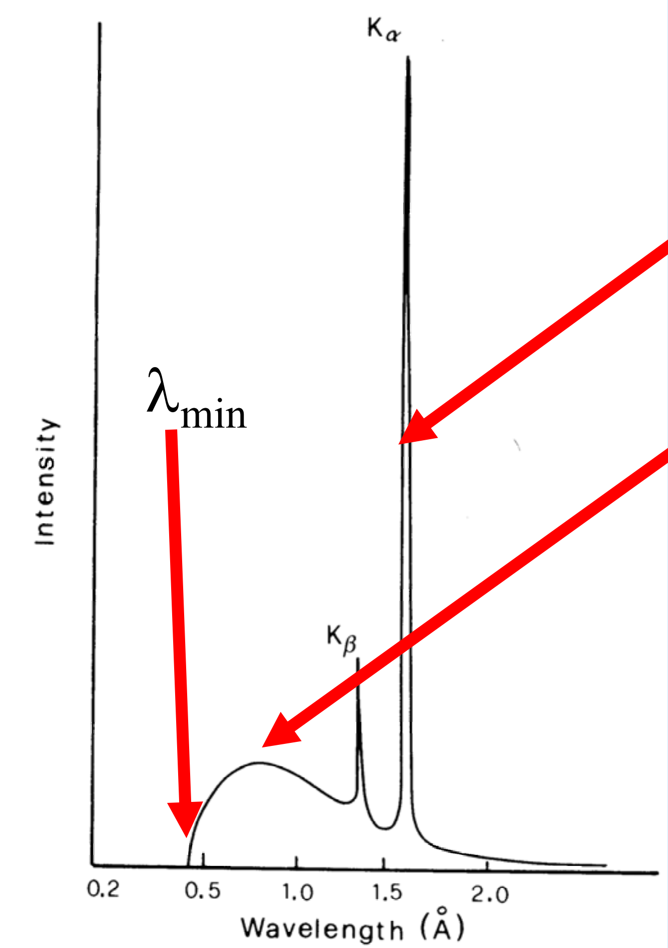


Fig. 4.2. Characteristic spectrum of copper superimposed on the white radiation spectrum. Notice the ratio of the relative intensities of the K_α and K_β lines.

Characteristic radiation

Bremstrahlung (white radiation)

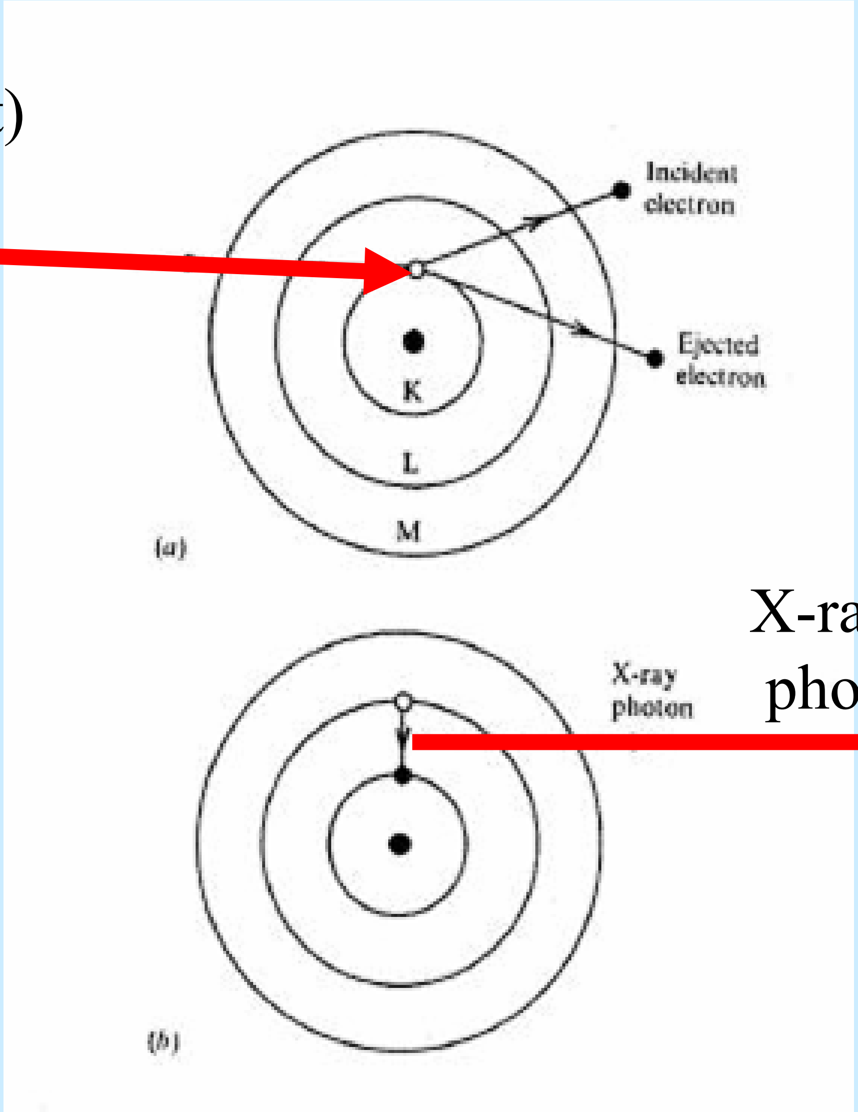
$E_{max} = E_0 = e \times V_0$

$E = (h \times c)/\lambda$

$$\lambda_{min}(A) = \frac{hc}{eV_0} = \frac{12.398}{V_0(kV)}$$

Characteristic X-ray radiation

Primary (incident) electron



X-ray (fluorescence) photon K_{α}

Selection Rules

- $n = 1, 2, 3….$ (principal quantum number), corresponds to K, L, M... shells

- $l = 0, 1, ..., n-1$ (orbital quantum number)

- $j =| l \pm s|$; $s = 1/2$ (spin-orbit coupling)

- $m_j = j, j-1, j-2, ..., -j$

- Transition only, when

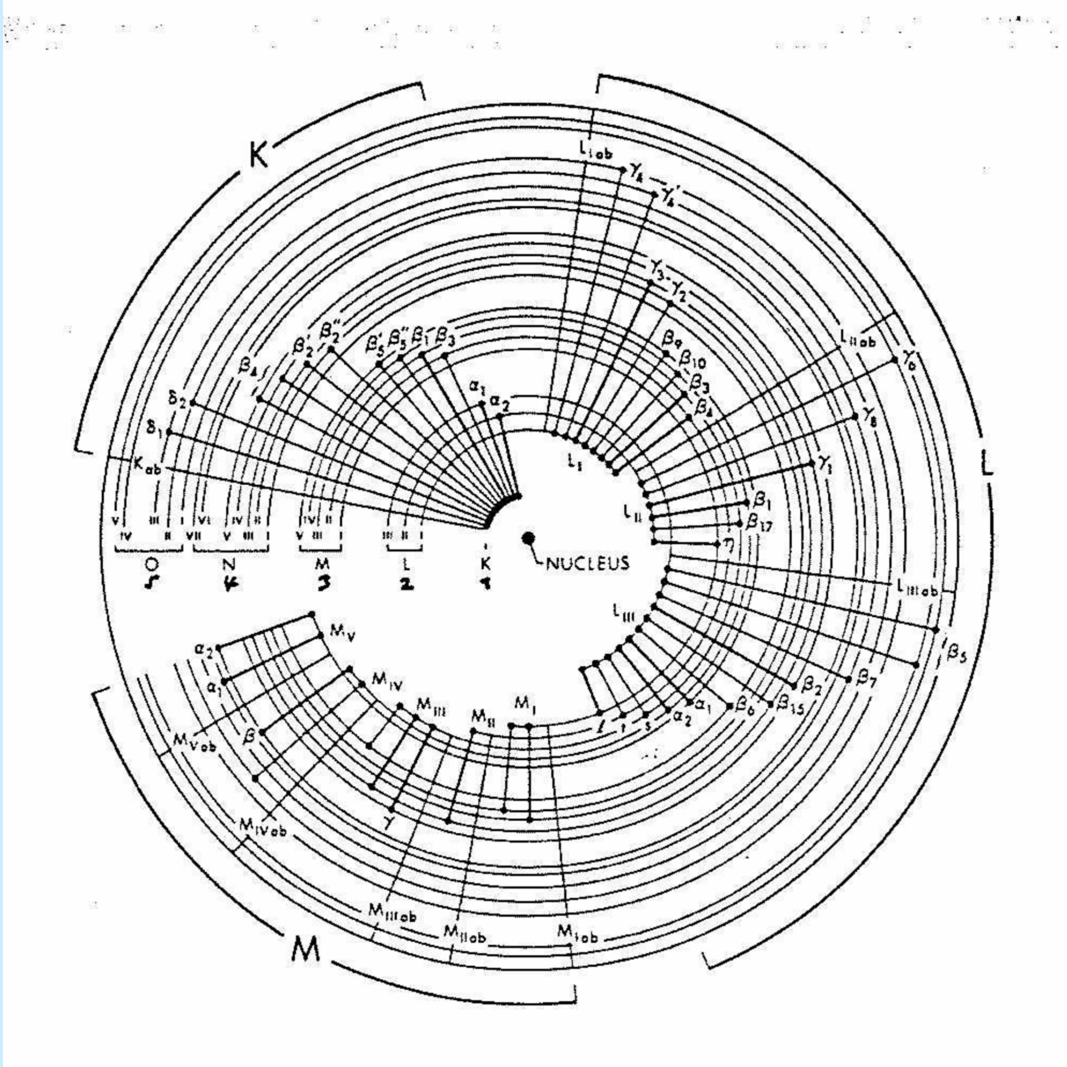
$\Delta n \geq 1$, $\Delta l = 1$, $\Delta j = 0$ or 1

Selection Rules

$M = 2J + 1$

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

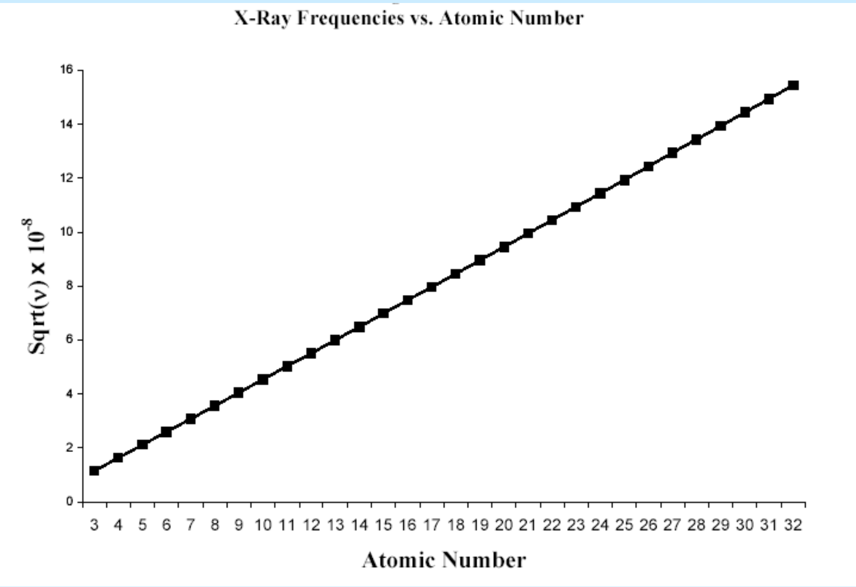
Allowed Transitions



Mosley's Law (for multiple electron atoms)

$1/\lambda = c\cdot(Z-\sigma)^2\cdot(1/n_1^2 - 1/n_2^2)$ $\sqrt{\ddot{\upsilon}}(K_\alpha) = \sqrt{\tfrac{3}{4}R}\ (Z-1)$

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



Decreasing wavelength λ with increasing Z

Characteristic Wavelengths

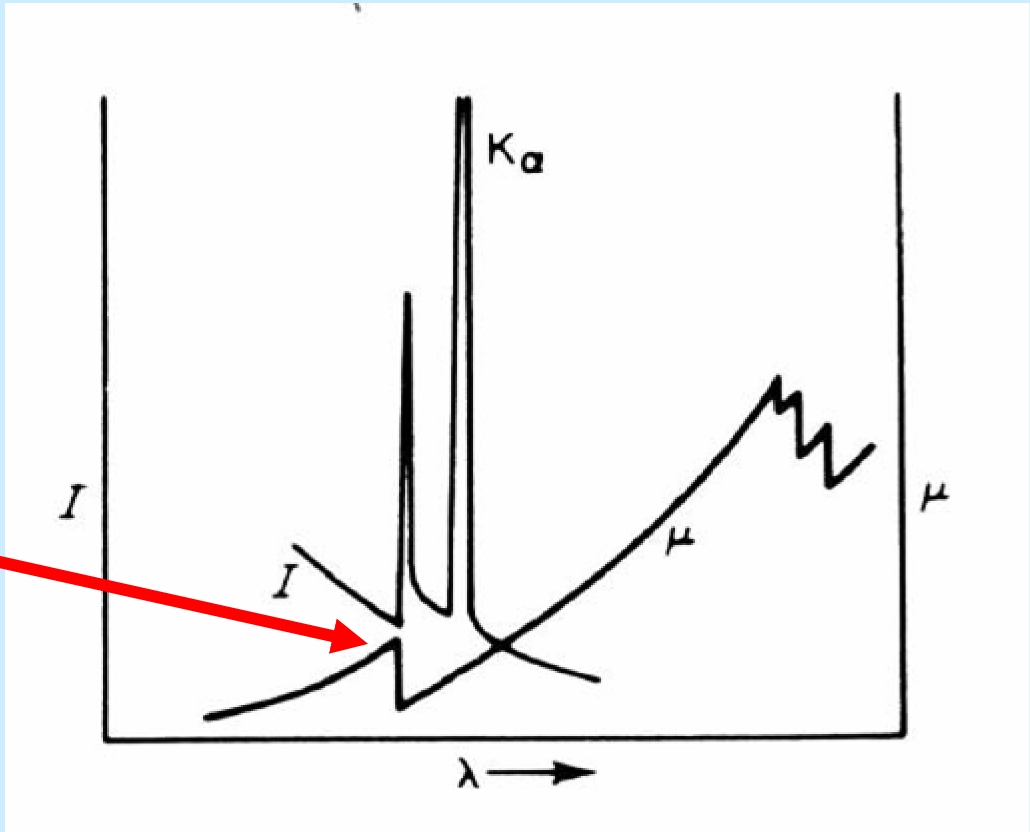
Element	$K_{\alpha 2}$	$K_{\alpha 1}$	K_{β}	K abs. edge
Cu	1.54433	1.54051	1.39217 1.38102	1.380
Mo	0.713543	0.70926	0.62099	0.61977
Ag	0.563775	0.559363	0.49701 0.48701	0.4858
W	0.213813	0.208992	0.17950	0.17837

X-ray Absorption

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

μ = absorption coefficient

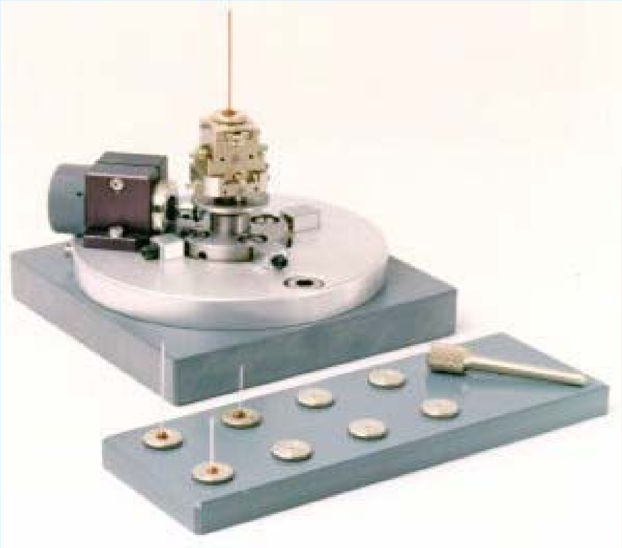
Absorption edge



Monochromatisation of X-rays

- Filters (Ni filter for Cu K_α)
- Crystal Monochromators

Sample Holders



Capillary

Transmission

Reflection

Detection of X-rays

Detectors

•convert energies of individual photons to electric current
•convert current into voltage pulses that are counted

•Film (in the linear range, Guinier, Debye-Scherrer, precession cameras)
•Gas Proportional Counter
•Si(Li) solid state detector (powder diffractometers)
•Scintillation counter (photocathode, dynodes, 4-circle diffractometer, Stoe powder diffractometer)
•Position Sensitive Detectors (1D or 2D, Stoe powder diffractometer)
•Image Plate Detectors (2D detection, Stoe IPDS)
•CCD Detectors (Bruker SMART system)

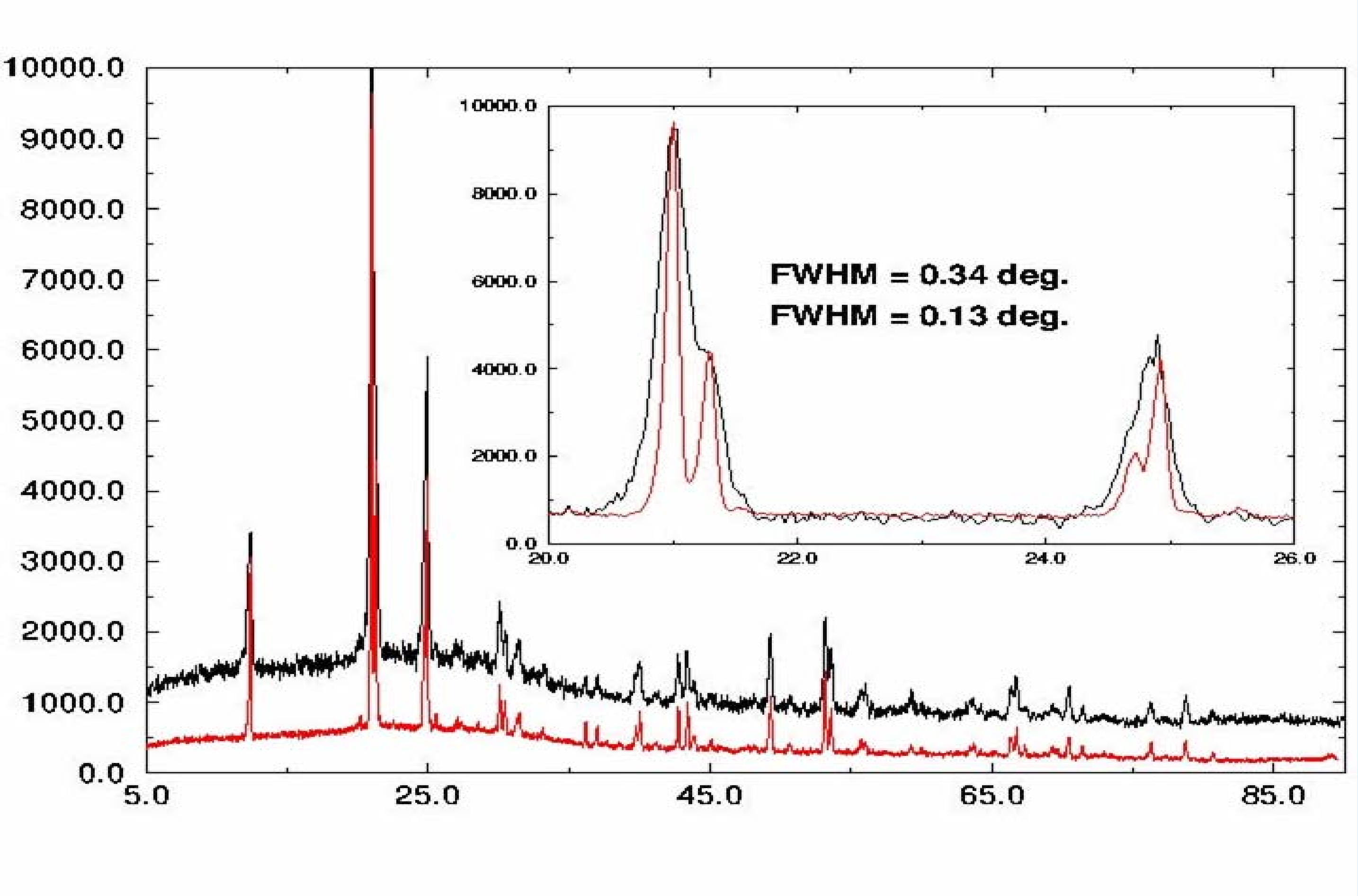
Image plate detectors

•Metal plate, 18 cm 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

Detector properties

- **quantum-counting efficiency**
- **linearity**
- **energy proportionality**
- **resolution**

Resolution

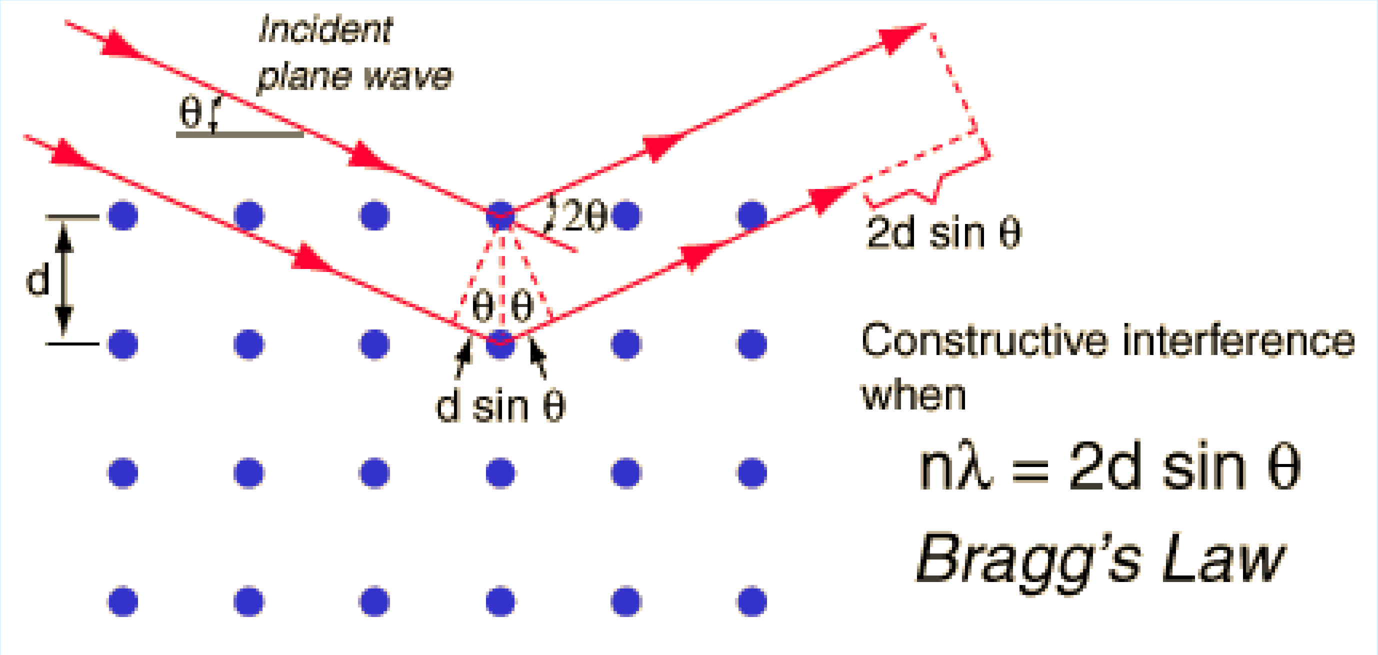


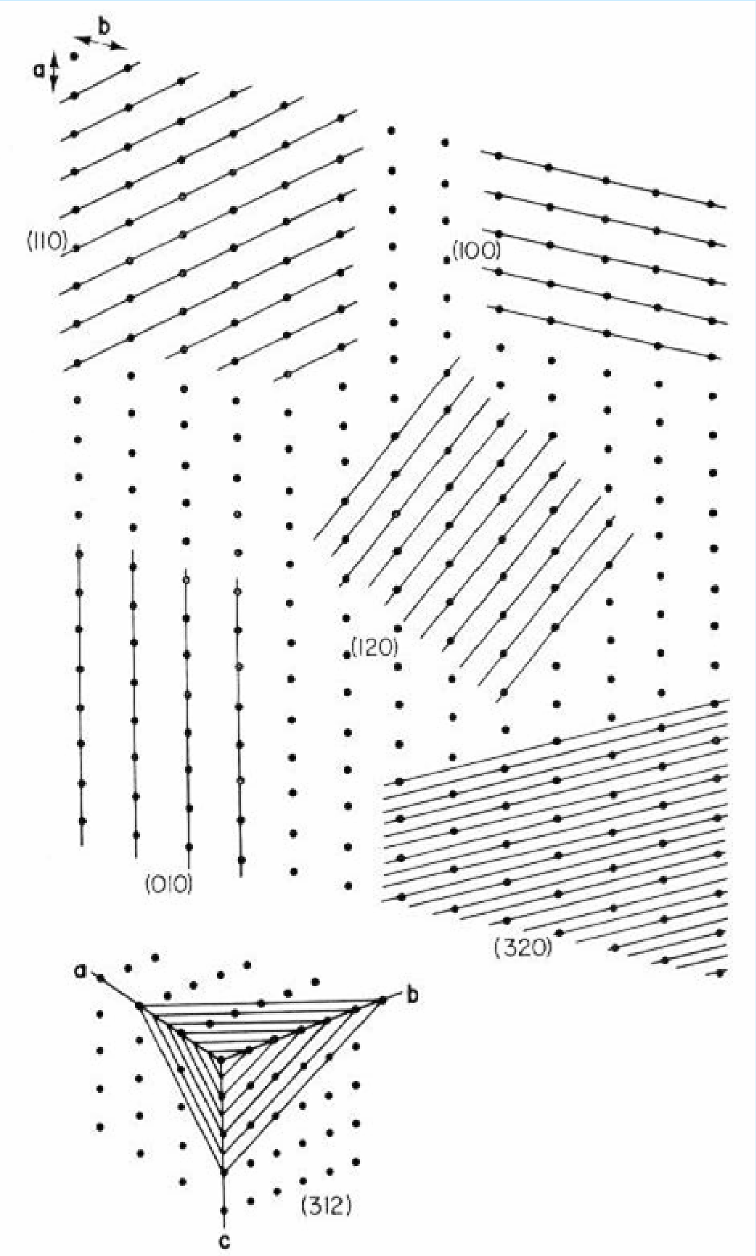
FWHM = 0.34 deg.
FWHM = 0.13 deg.
10000.0
9000.0
8000.0
7000.0
6000.0
5000.0
4000.0
3000.0
2000.0
1000.0
0.0
5.0
25.0
45.0
65.0
85.0
10000.0
8000.0
6000.0
4000.0
2000.0
0.0
20.0
22.0
24.0
26.0

X-ray Powder Diffraction

William Bragg ***(1912)***

$$n.\lambda = 2\ d \sin \Theta$$

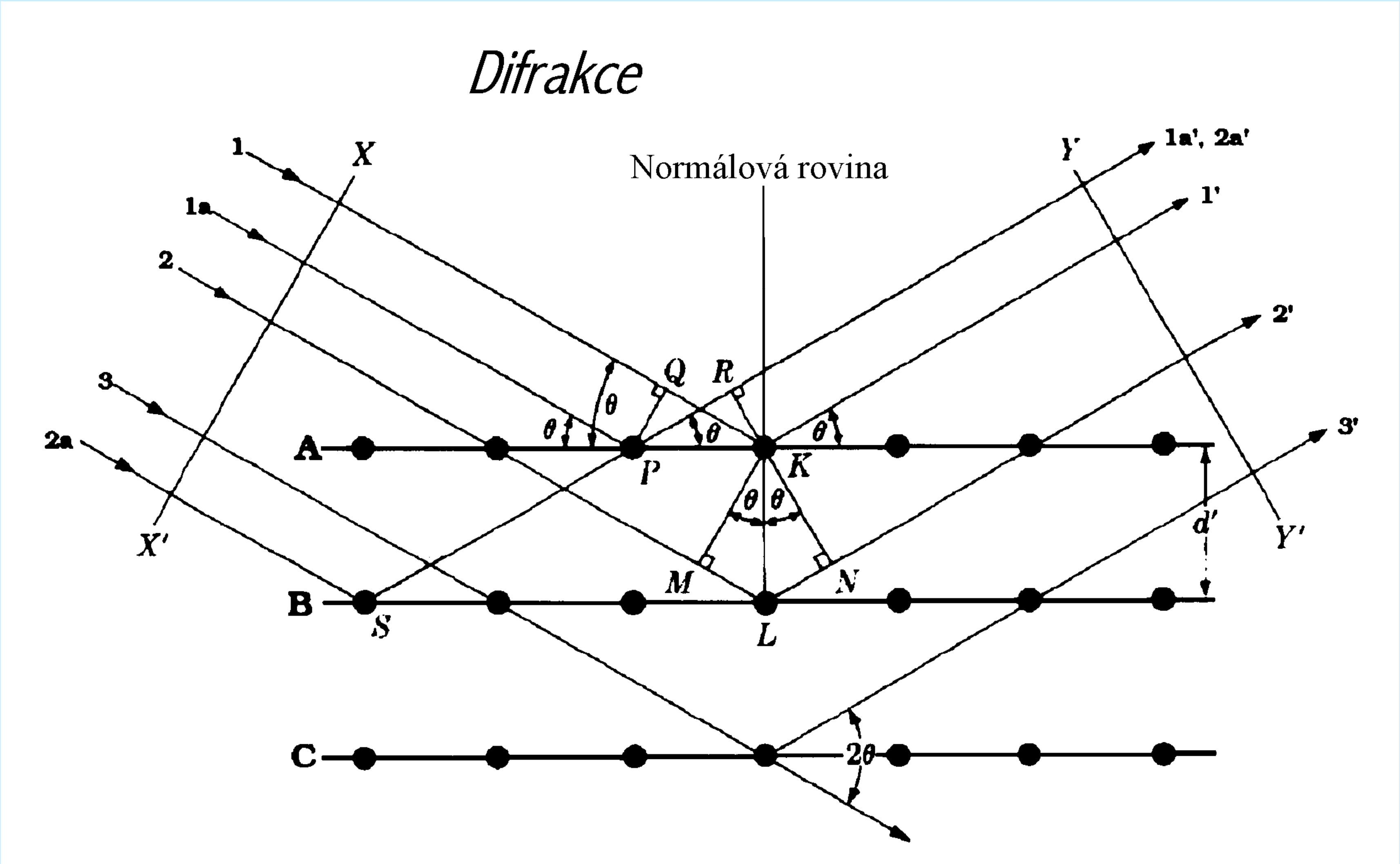




a
b
(110)
(100)
(120)
(010)
(320)
a
b
c
(312)

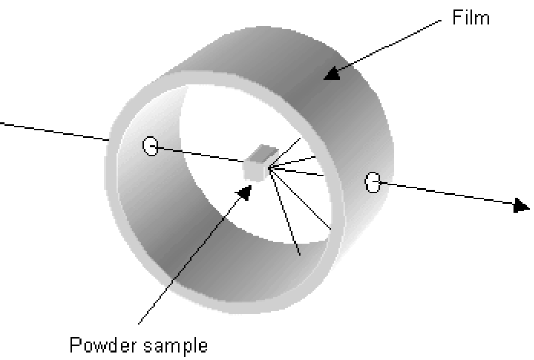
Laue method → Single crystals

Debye-Scherrer, diffractometers → polycrystalline

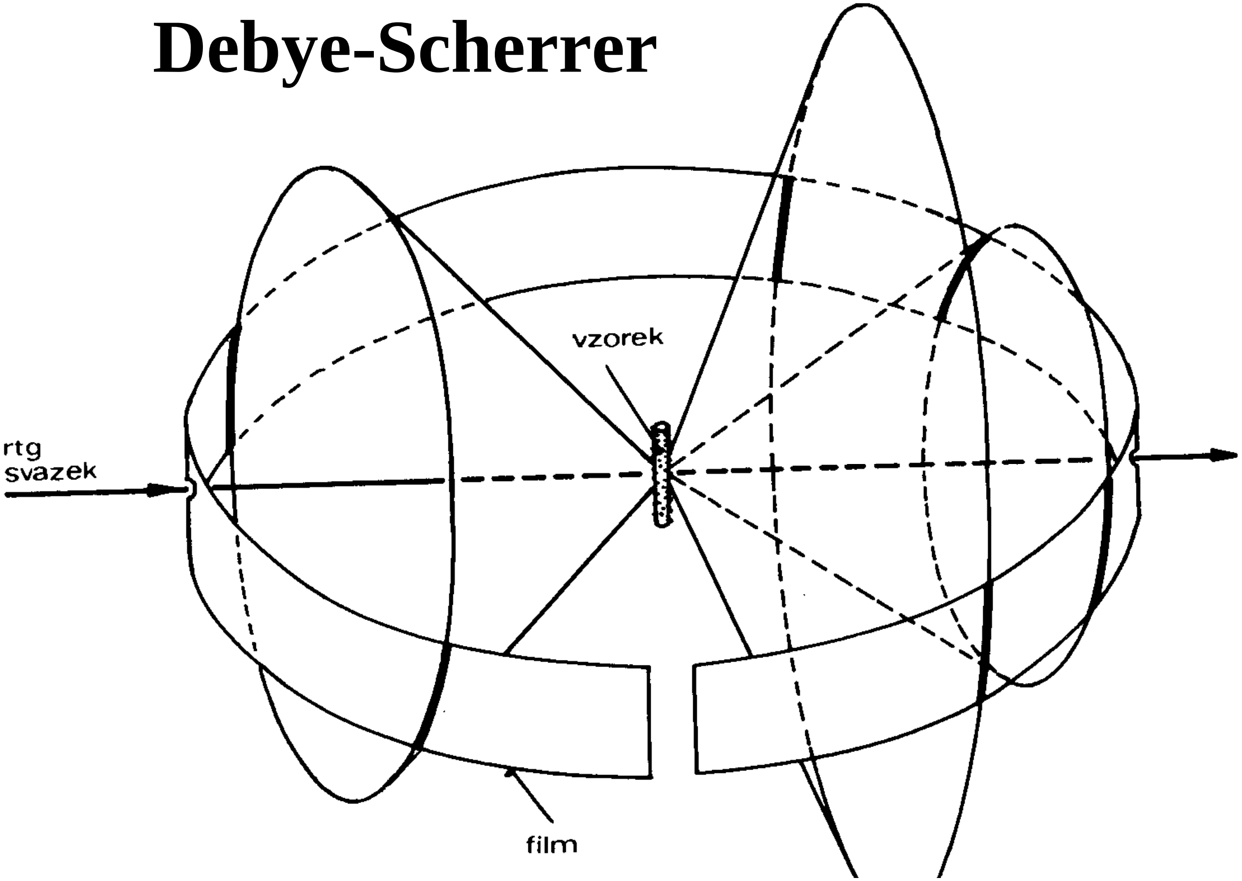


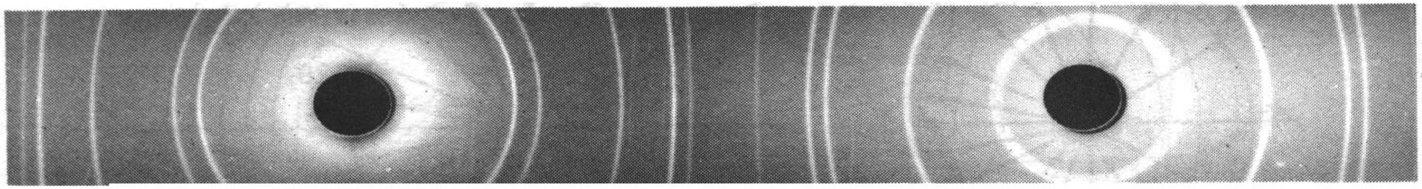
Different Geometries of Powder Diffractometers

- Debye-Scherrer
- Bragg-Brentano
- Guinier



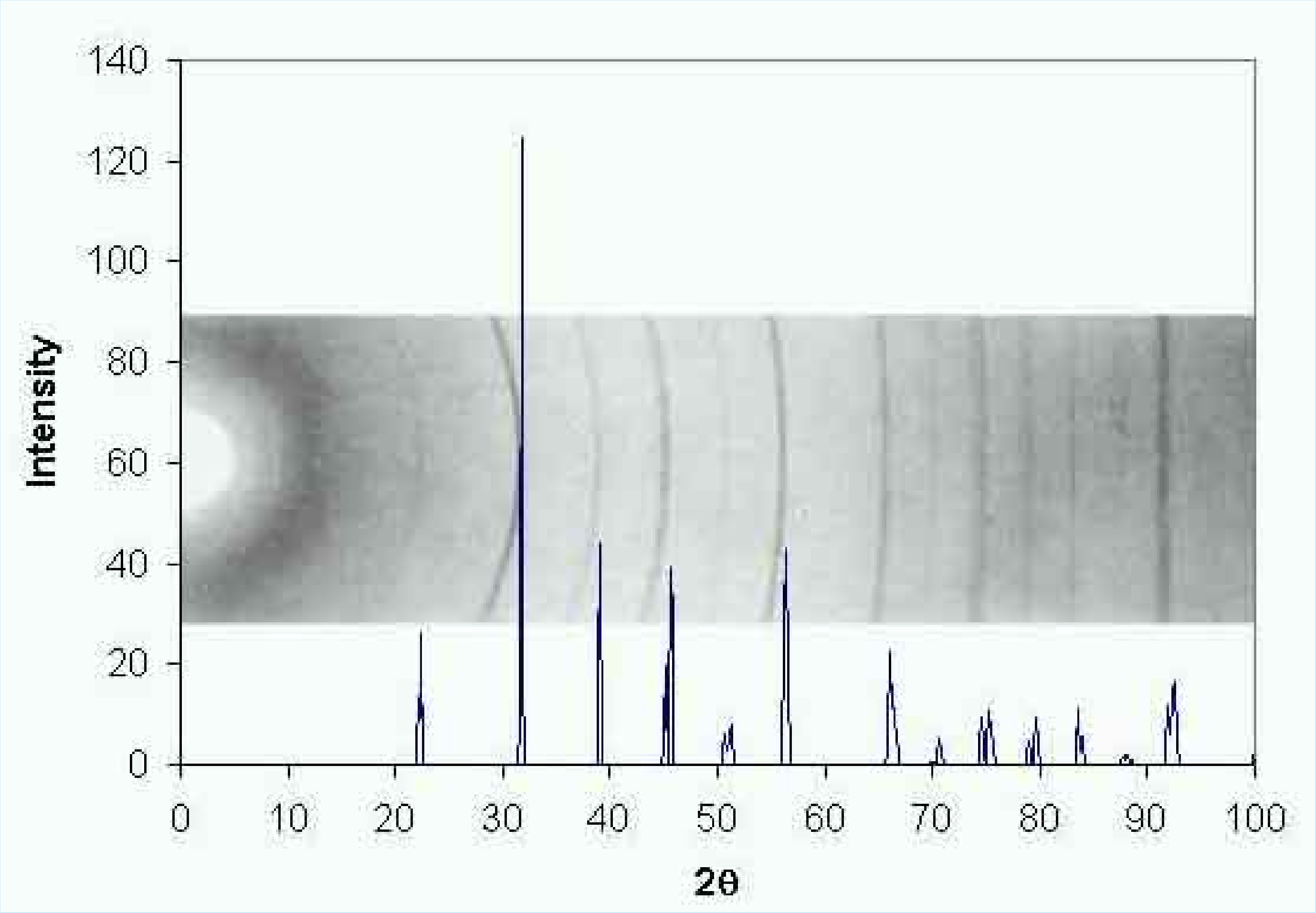
Debye-Scherrer



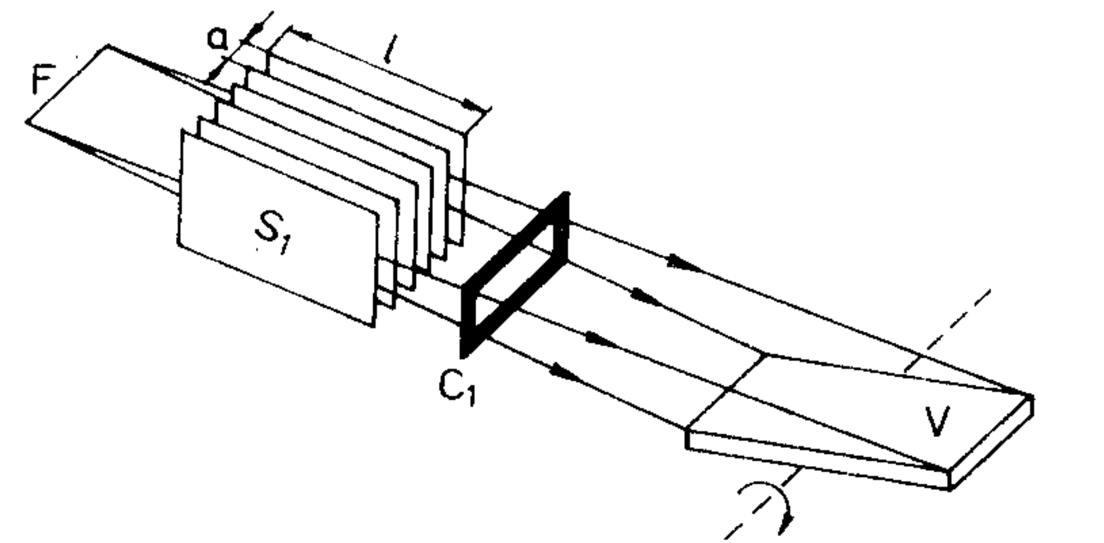


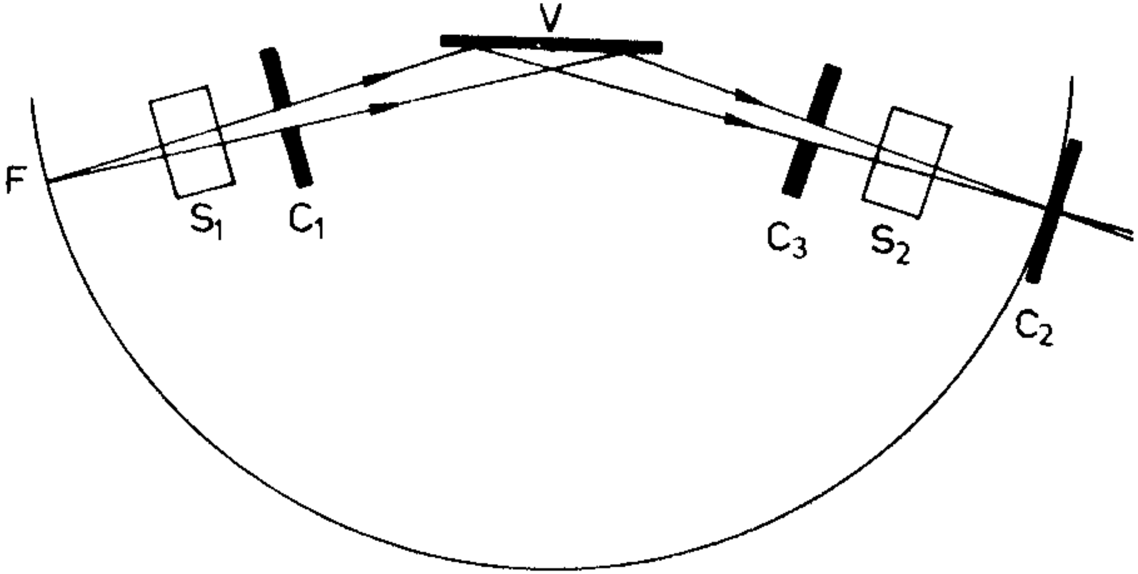
Debyegram práškového stříbra ($\lambda = 1{,}54 \,.\, 10^{-10}$ m)

Debye-Scherrer



Bragg-Brentano

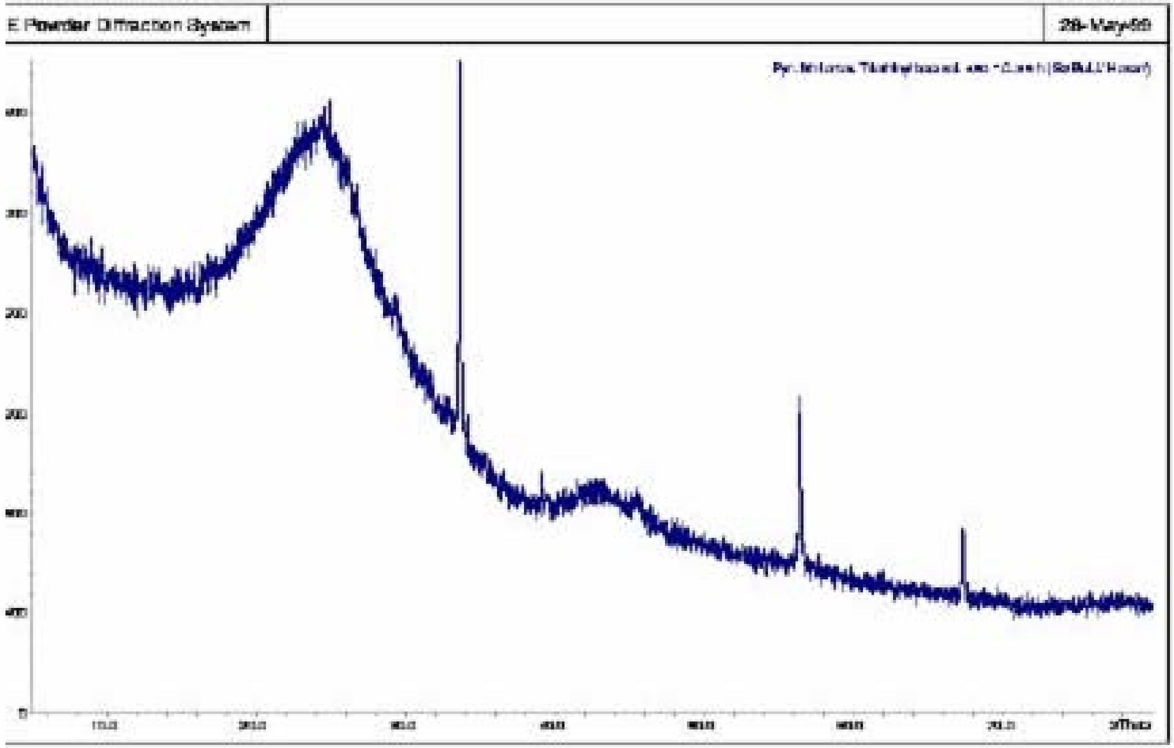




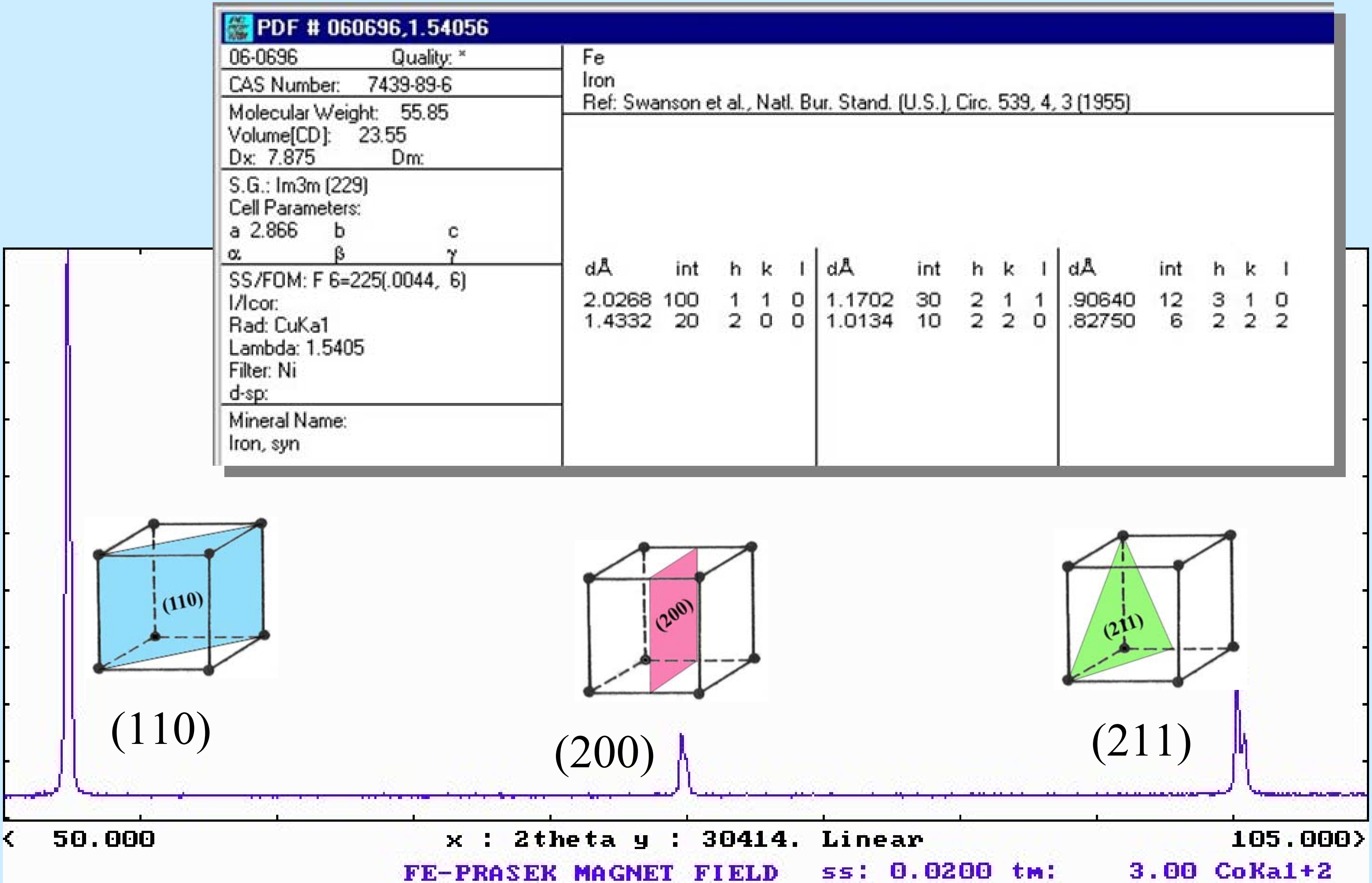
Information Extracted from Diffraction Experiments

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

Crystalline and Amorphous Phases



X-ray powder diffraction pattern of Fe



PDF # 060696,1.54056

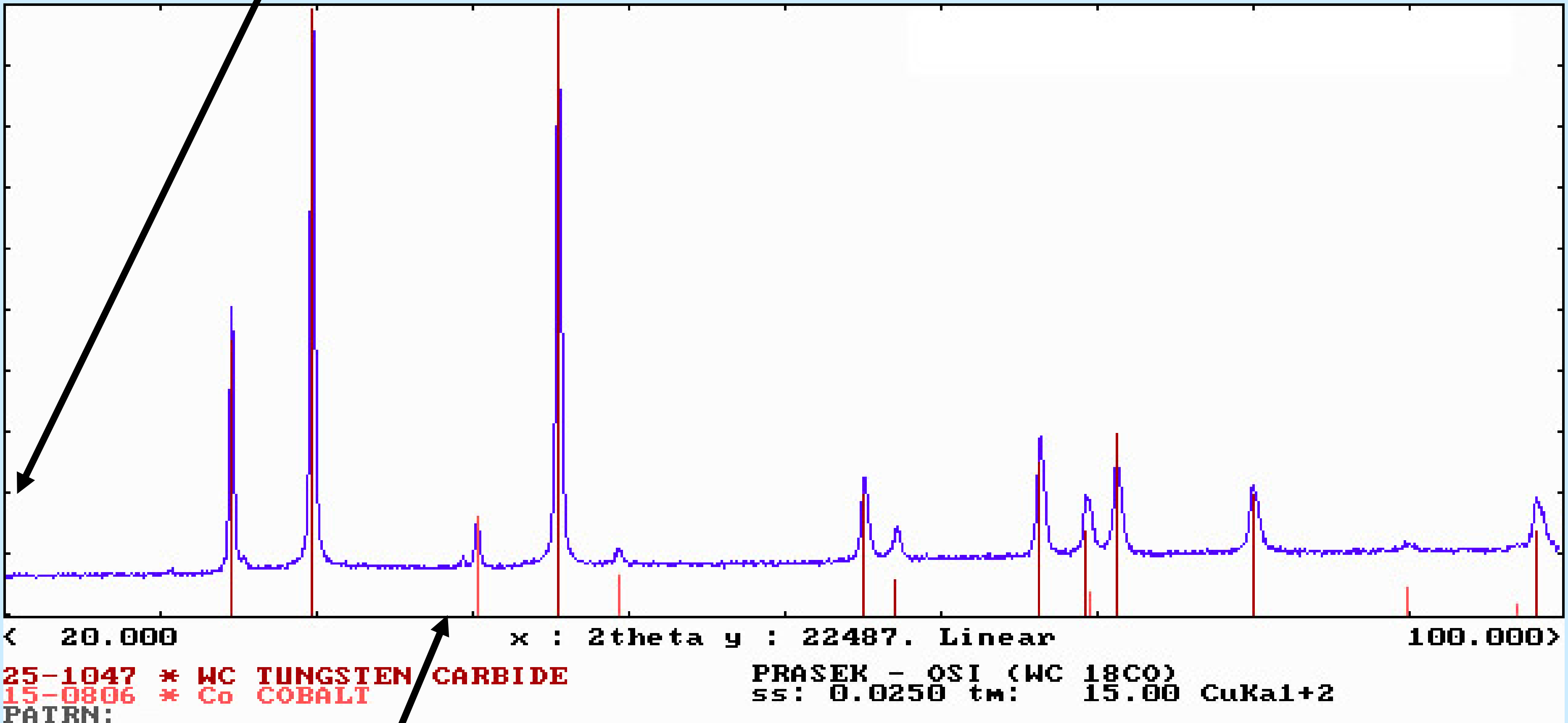
06-0696 Quality: *
CAS Number: 7439-89-6
Molecular Weight: 55.85
Volume[CD]: 23.55
Dx: 7.875 Dm:
S.G.: Im3m (229)
Cell Parameters:
a 2.866 b c
α β γ
SS/FOM: F 6=225(.0044, 6)
I/Icor:
Rad: CuKa1
Lambda: 1.5405
Filter: Ni
d-sp:
Mineral Name:
Iron, syn

Fe
Iron
Ref: Swanson et al., Natl. Bur. Stand. (U.S.), Circ. 539, 4, 3 (1955)

dÅ	int	h	k	l	dÅ	int	h	k	l	dÅ	int	h	k	l
2.0268	100	1	1	0	1.1702	30	2	1	1	.90640	12	3	1	0
1.4332	20	2	0	0	1.0134	10	2	2	0	.82750	6	2	2	2

Quantity

More complicated, volume fraction



Quality

$$d = \lambda / 2 \sin \Theta$$

Line position is given by interplanar distance d and wavelenght λ

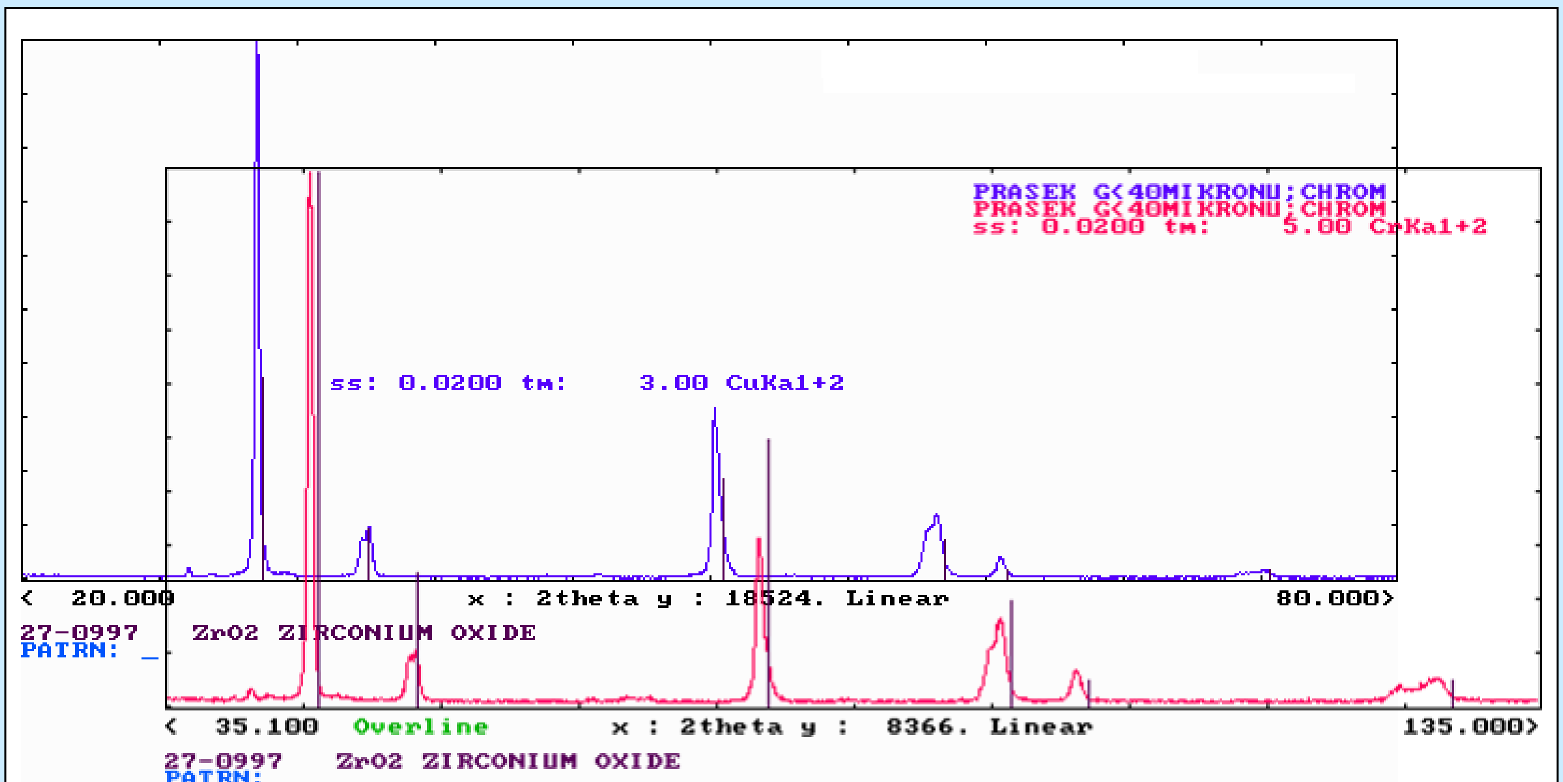
Selecting radiation

Anode	Wavelength [nm]			Beta filter
	$K\alpha_1$ [100]	$K\alpha_2$ [50]	$K\beta_1$	
Cr	0.228970	0.229361	0.208487	V
Fe	0.193604	0.193998	0.175661	Mn
Co	0.178897	0.179285	0.162079	Fe
Cu	0.154056	0.154439	0.139222	Ni
Mo	0.070930	0.071359	0.063229	Zr

$d = \lambda / 2 \sin \Theta$ ... longer λ ... better multiplet separation
... shorter λ ... more lines

Bcc crystal, Cu radiation

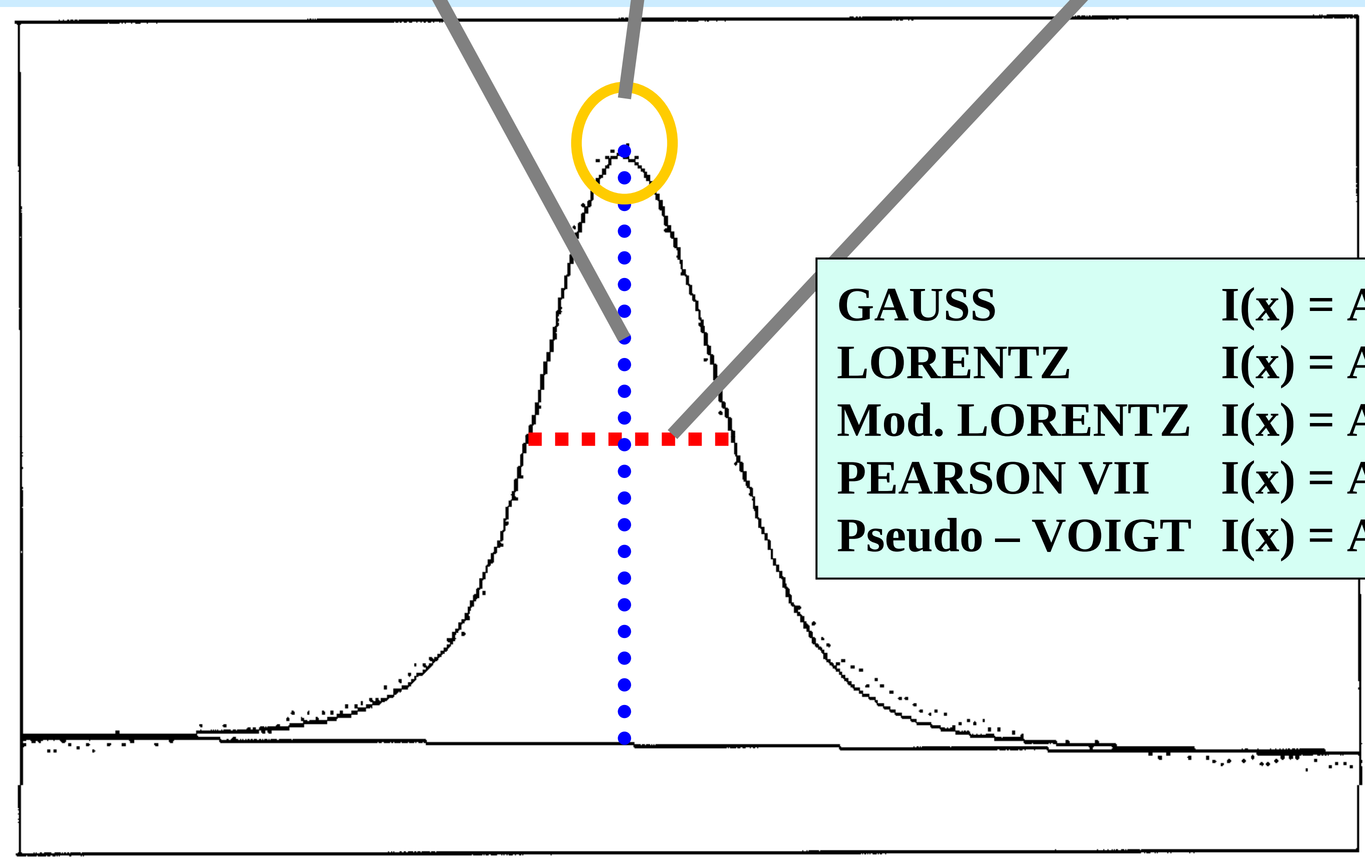
a = 1.5 nm --> 2Θ = 11.8
a = 1.2 nm --> 2Θ = 14.8
a = 0.9 nm --> 2Θ = 19.7
a = 0.6 nm --> 2Θ = 29.8
a = 0.3 nm --> 2Θ = 61.8



LINE HEIGHT
- integral intensity
- quantitative analysis
- texture

LINIE POSITION
- qualitative (phase) analysis
- lattice macrodistortions

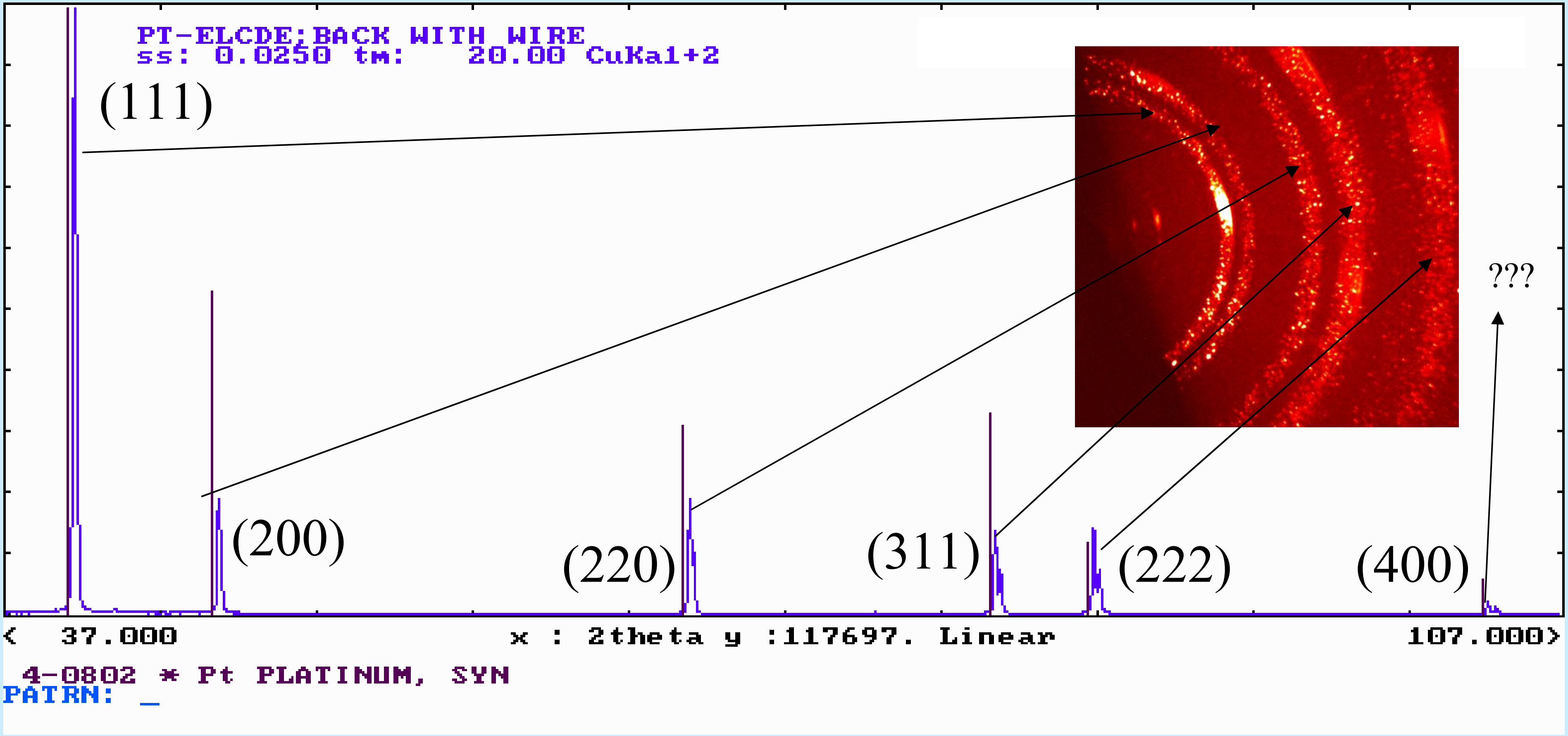
LINIE WIDTH
- size of diffracting domains
- lattice microdistortions



GAUSS	**$I(x) = A \exp(-x^2/a^2)$**
LORENTZ	**$I(x) = A \exp[1+(x^2/a^2)]^{-1}$**
Mod. LORENTZ	**$I(x) = A \exp[1+(x^2/a^2)]^{-2}$**
PEARSON VII	**$I(x) = A \exp[1+(x^2/a^2)]^{-n}$**
Pseudo – VOIGT	**$I(x) = A [cL(x) + (1-c)G(x)]$**

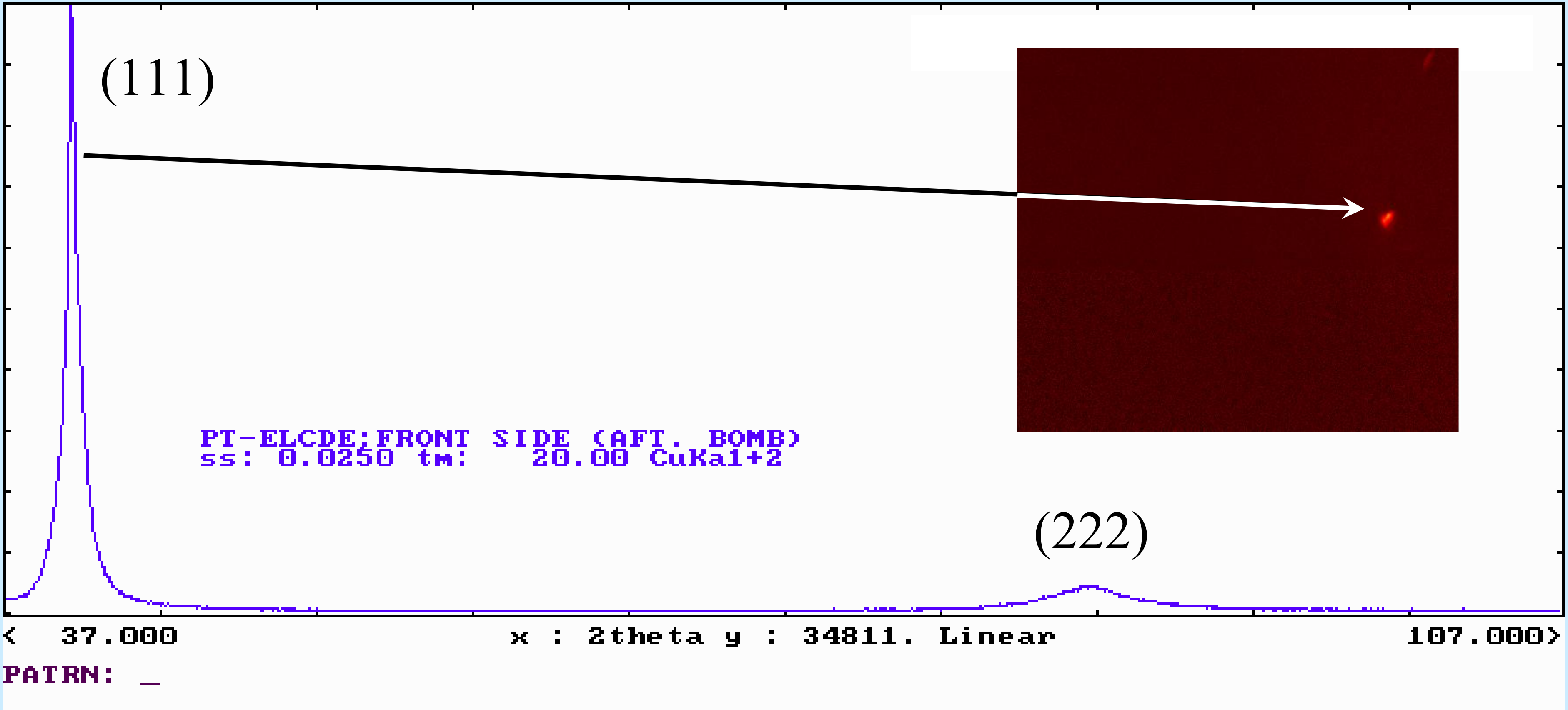
Comparison of Debye-Scherrer versus diffractometer

Polycrystalline sample



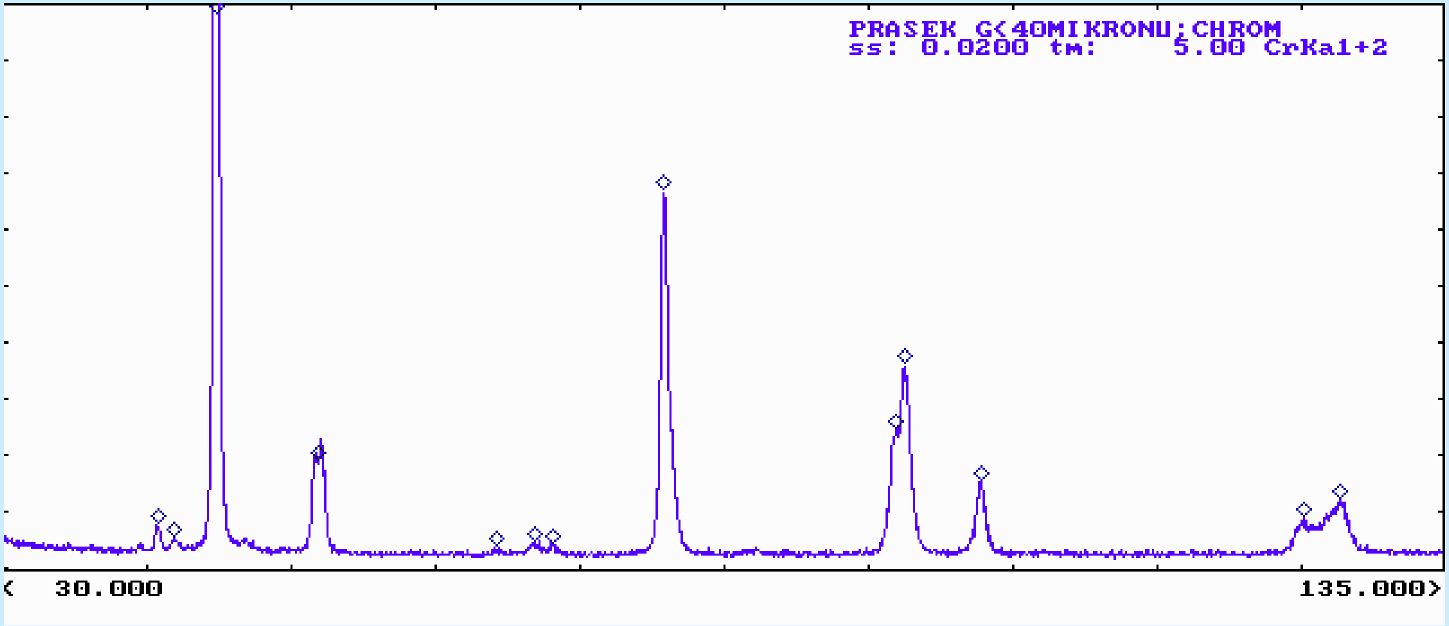
Comparison of Debye-Scherrer versus diffractometer

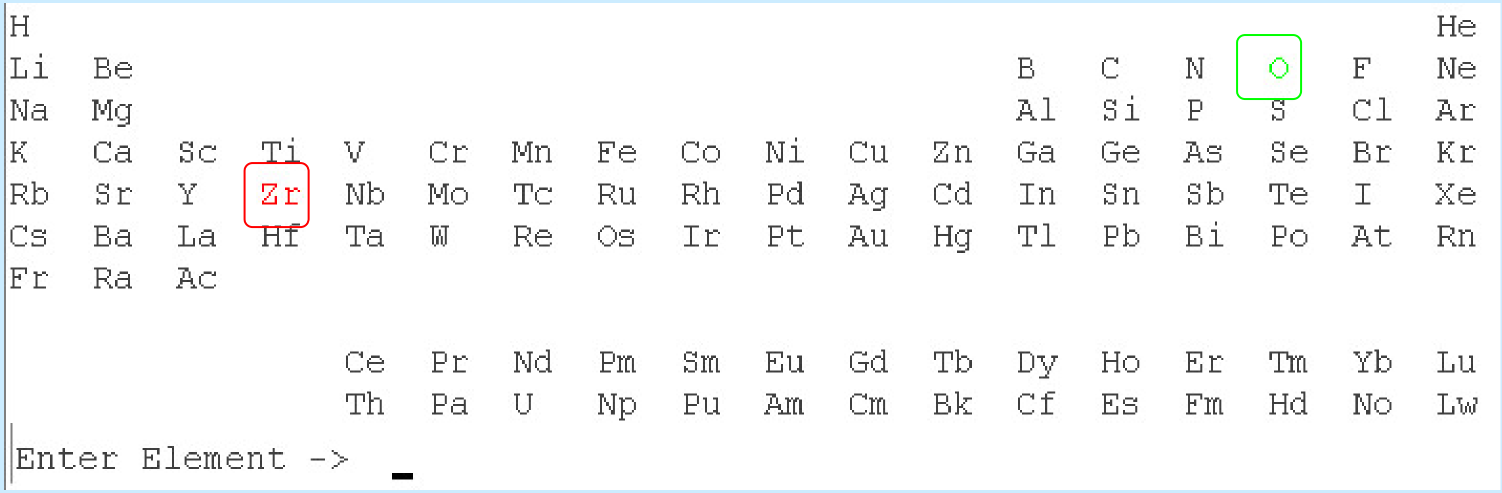
Single crystal



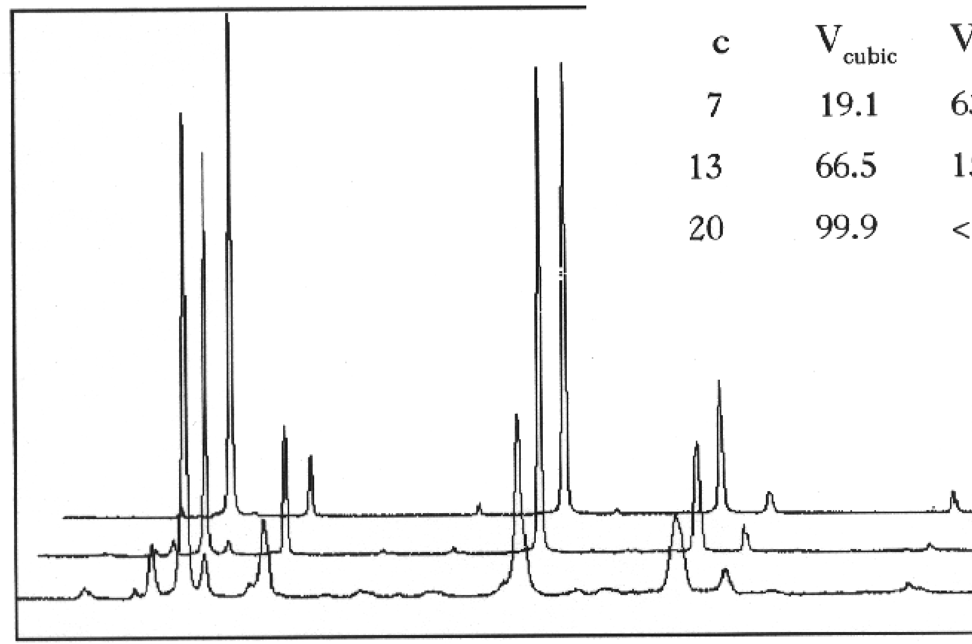
Phase analysis

$ZrO_2 + Y_2O_3$

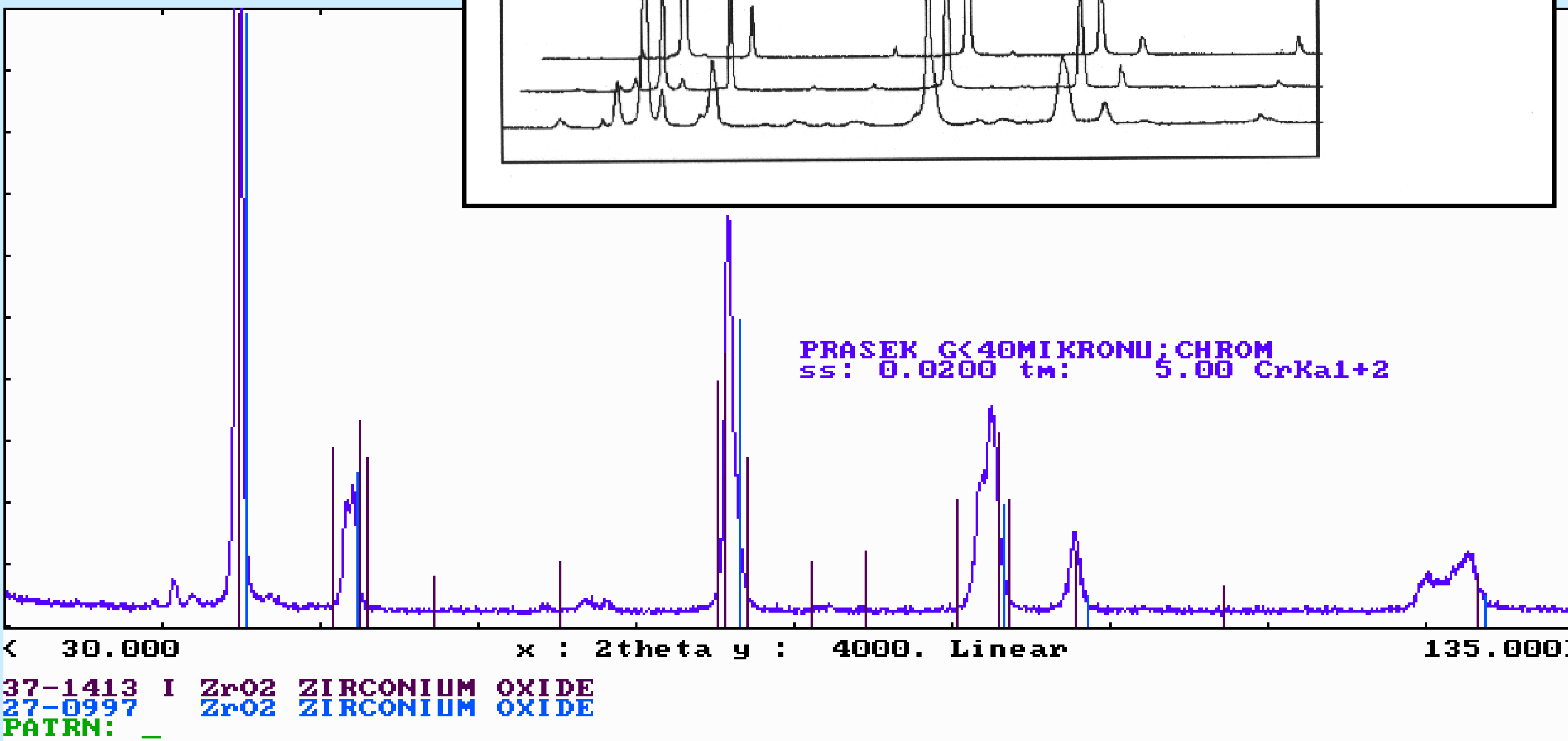




Results of phase analysis



c	V_{cubic}	V_{tetra}	V_{monok}
7	19.1	63.5	17.4
13	66.5	15.7	17.8
20	99.9	<0.1	<0.1



Databases

- ICSD (Karlsruhe, inorganics, single crystal data)
- CSD (Cambridge, organics, organometallics, sc data)
- NRCC CRYSTMET (metals)
- PDB (proteins, Brookhaven)
- NIST (NBS)
- JCPDS = ICDD (PDF files, 60000 patterns)

Which of these is *not* involved in the diffraction of X-rays through a crystal?

a	Electron transitions
b	Crystallographic planes
c	Nuclear interactions
d	Constructive interference

What is the *largest* wavelength of radiation that will be diffracted by a lattice plane of the interplanar spacing *d*?

a	$0.5d$
b	d
c	$2d$
d	No limit