Diffraction and Electron Microscopy

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Contents

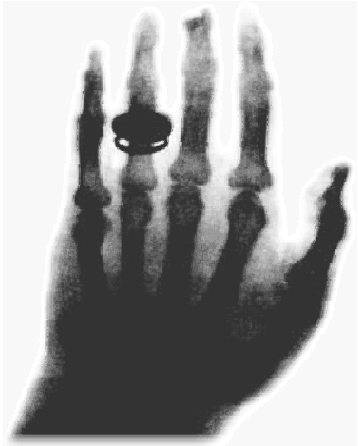
1. A short history

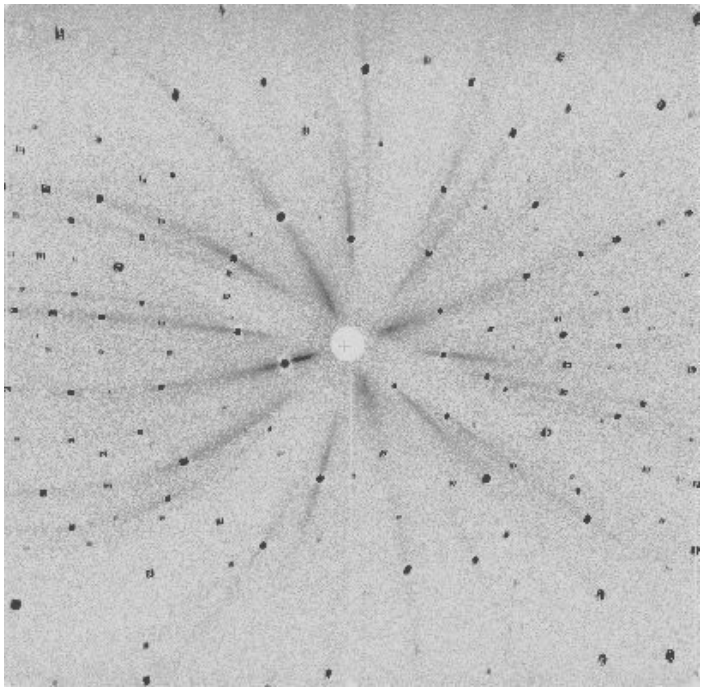
1895 W.C. Röntgen, discovery of X-rays

1901 Nobel prize for physics

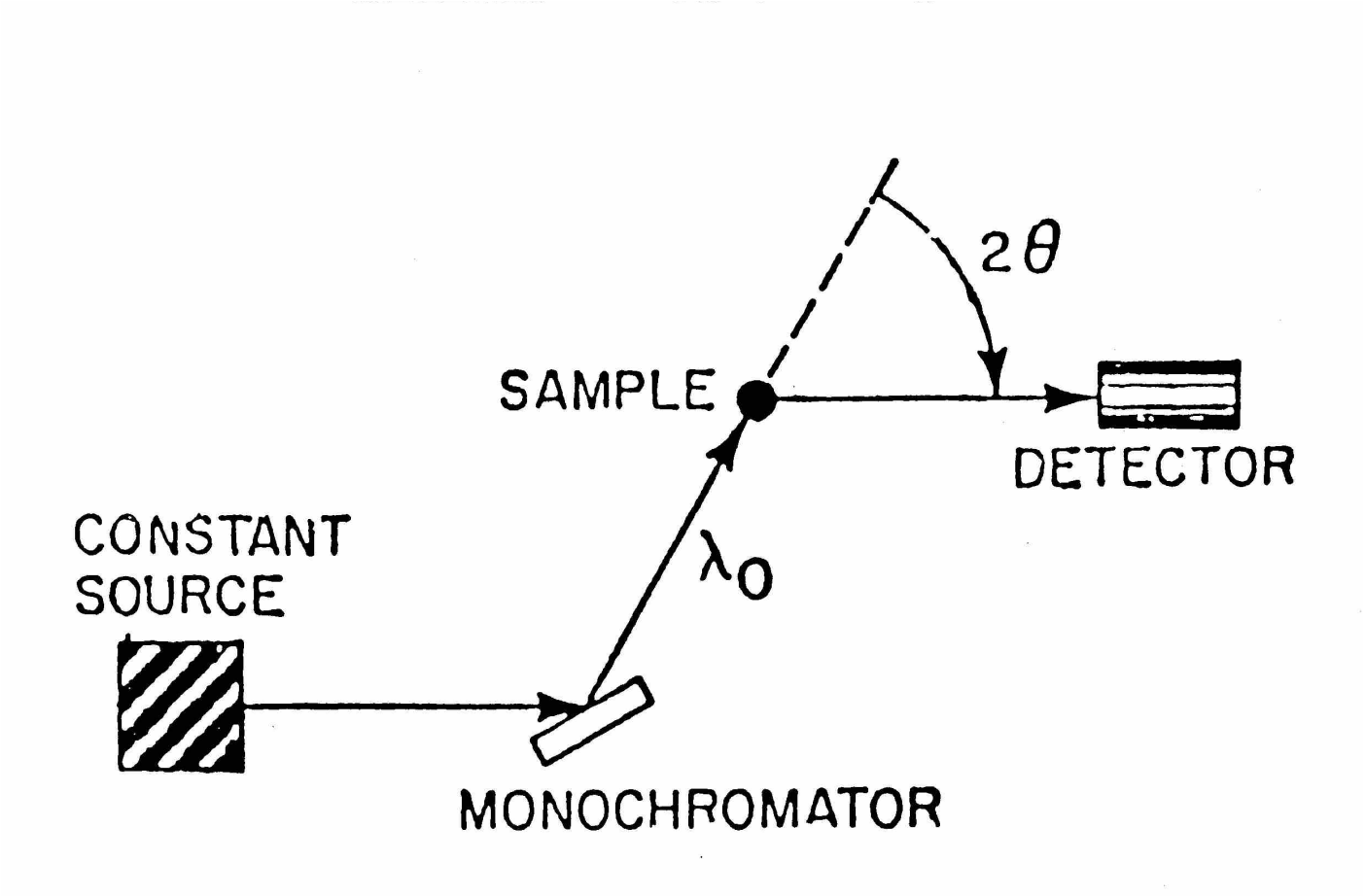
1912 M. von Laue, diffraction experiments on crystals

1914 Nobel prize for physics





2. Diffraction



elastic scattering

$\Delta E = 0$

λ constant

2. Diffraction

		interaction with	
i) wave	X-ray	electrons	XRD
	neutron	atomic nuclei	ND
		magnetic moments	
	electron	electrons	TEM

ii) grating crystalline material (sample)

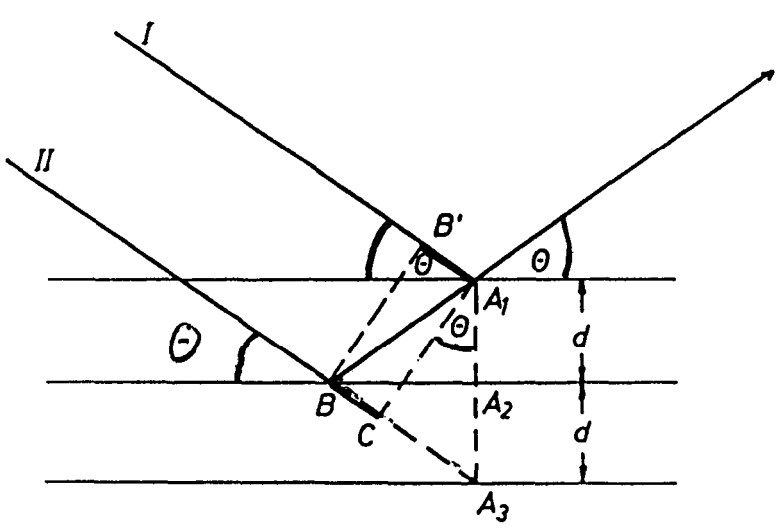
iii) elastic scattering ($\Delta E = 0$)

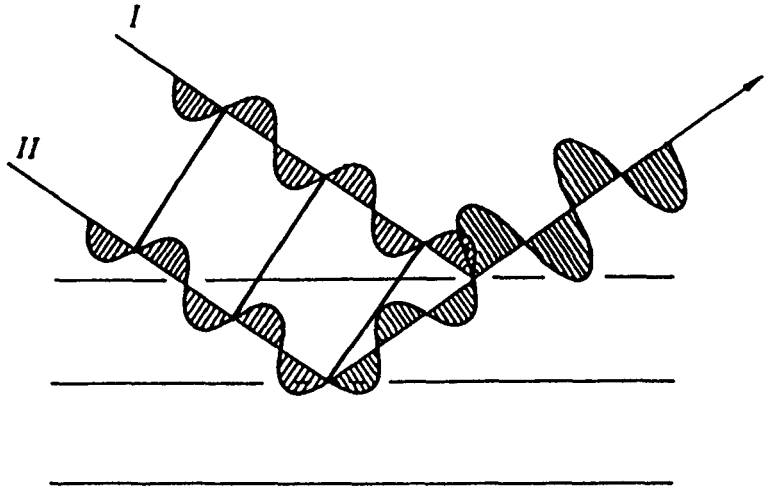
iv) interference of scattered waves

diffraction angle (2θ) $\rightarrow$ lattice parameters (unit cell)

reflection intensity (I_{hkl}) $\rightarrow$ atoms (element, site, etc.)

2. Bragg's law





interference of diffracted waves

B'-A_1 = B-C

B-A_1 = B-A_3

phase shift (B-A_1)-(B'-A_1) = C-A_3 = n λ

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

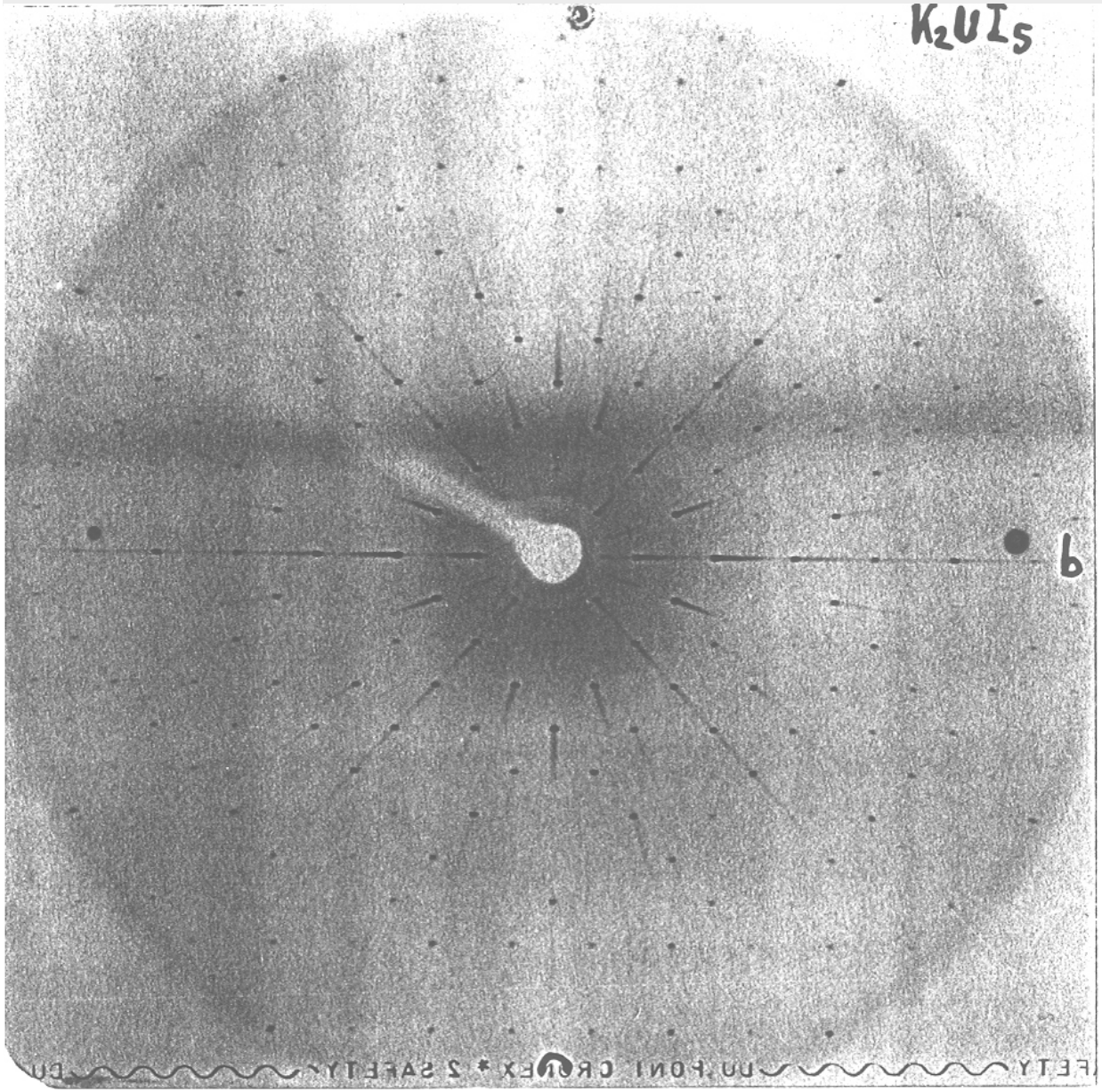
$n \lambda = 2 d \sin\theta$

d = layer distance

λ = wave length

n = 1

3. Single crystal diffraction

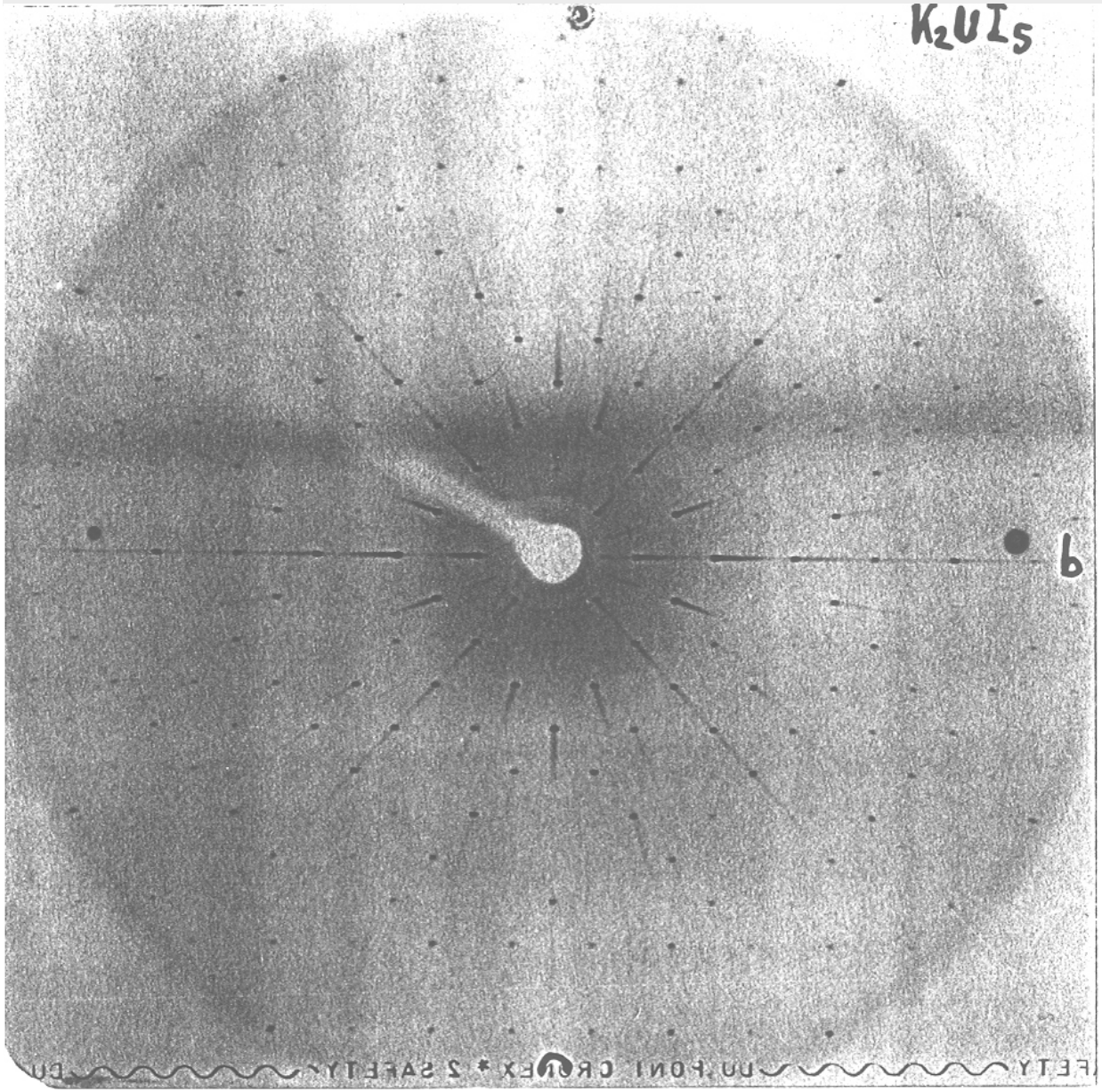


diffraction pattern
(here: (0kl) plane)

position of reflections
→ lattice parameters
(here: b, c, α)

intensity I_{hkl}
→ atoms in unit cell

3. Single crystal diffraction

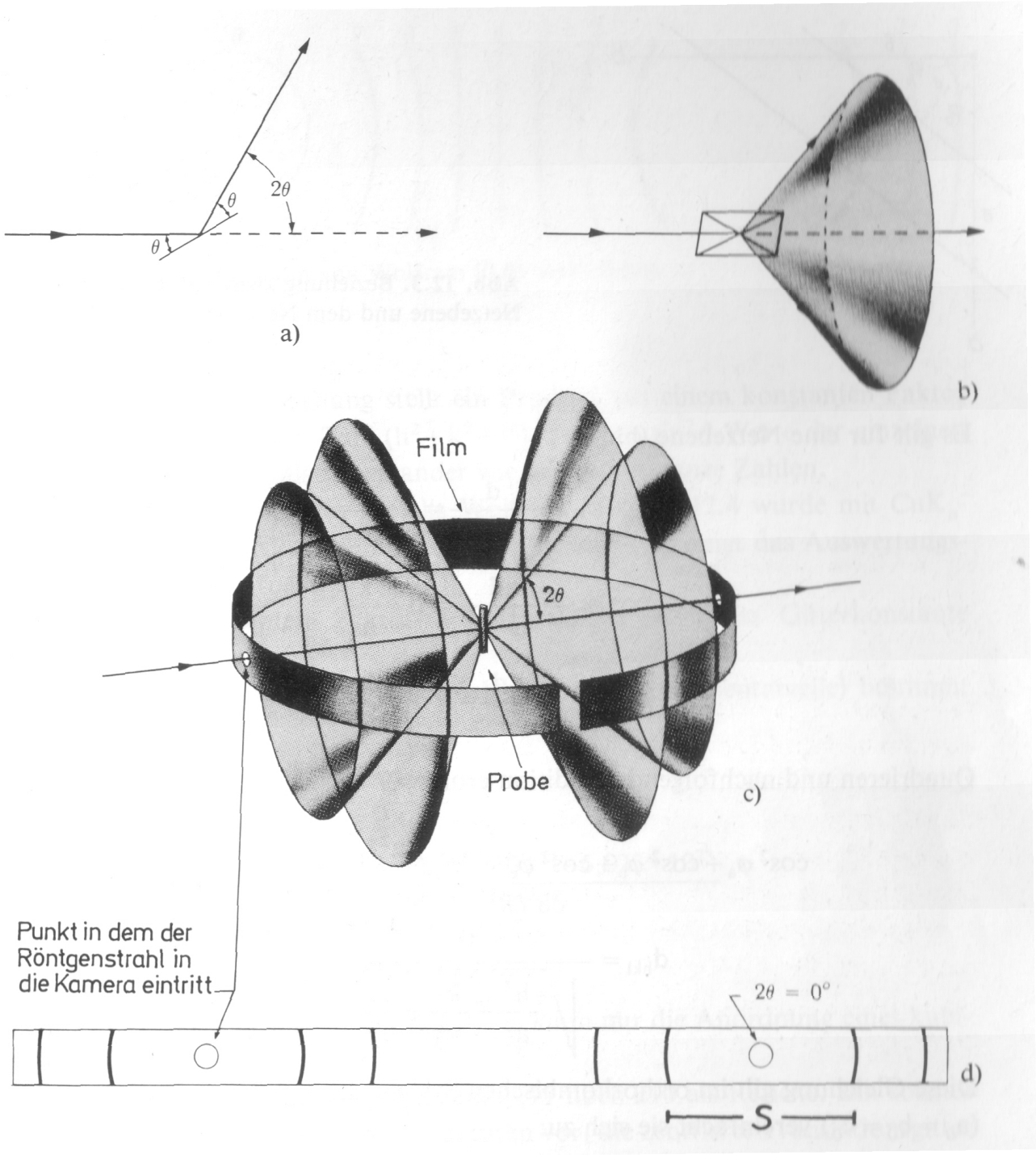


reflections with $I_{hkl}=0$
$\rightarrow$ symmetry

extinction rules
0kl with k+l=2n
(n glide plane $\perp$ a)

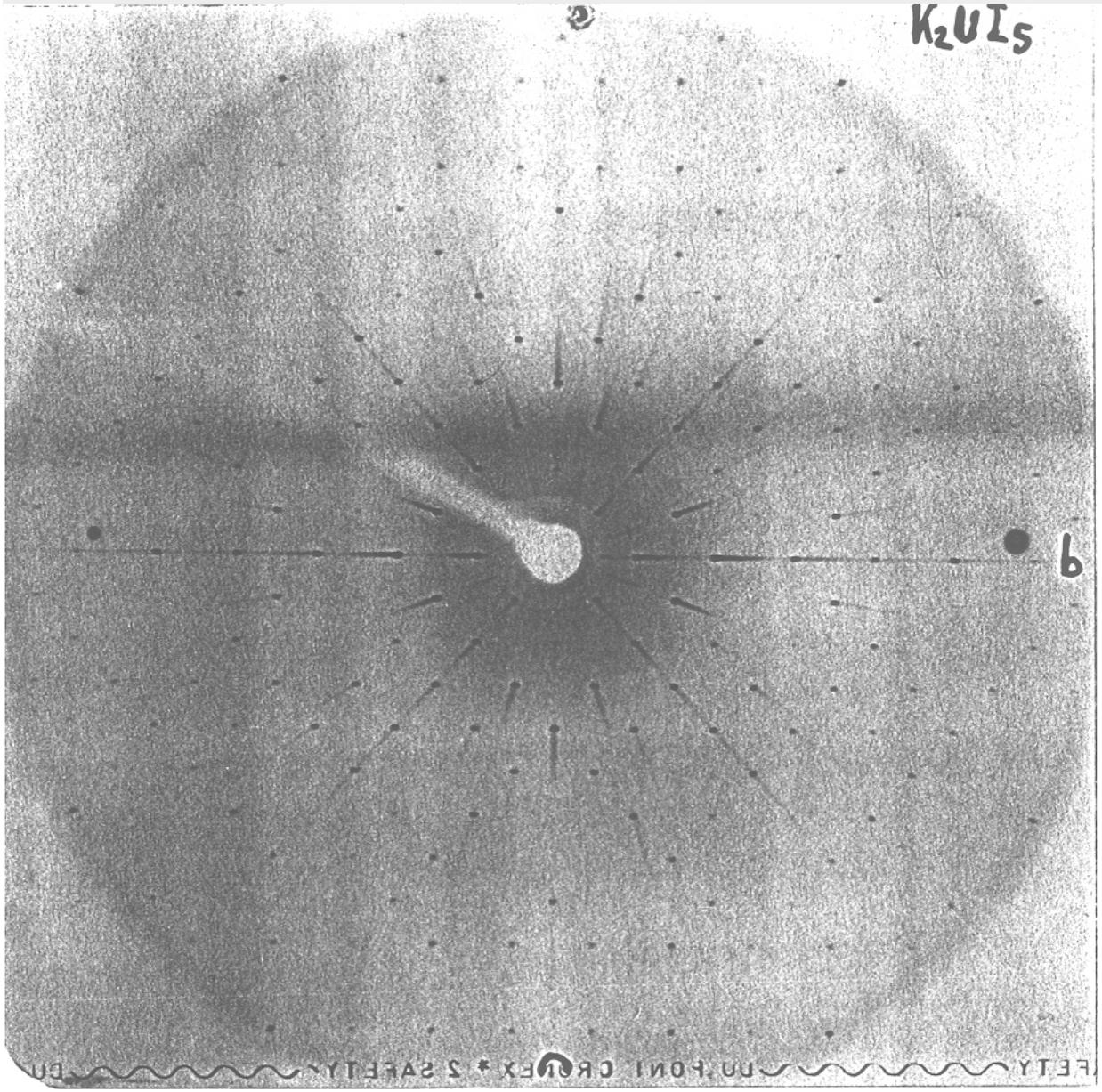
0k0 with k=2n
00l with l=2n
(2_1 screw axes
along b and c)

$\rightarrow$ space group
(here: Pnma =
P 2_1/n 2_1/m 2_1/a)



From
single crystal
to
powder

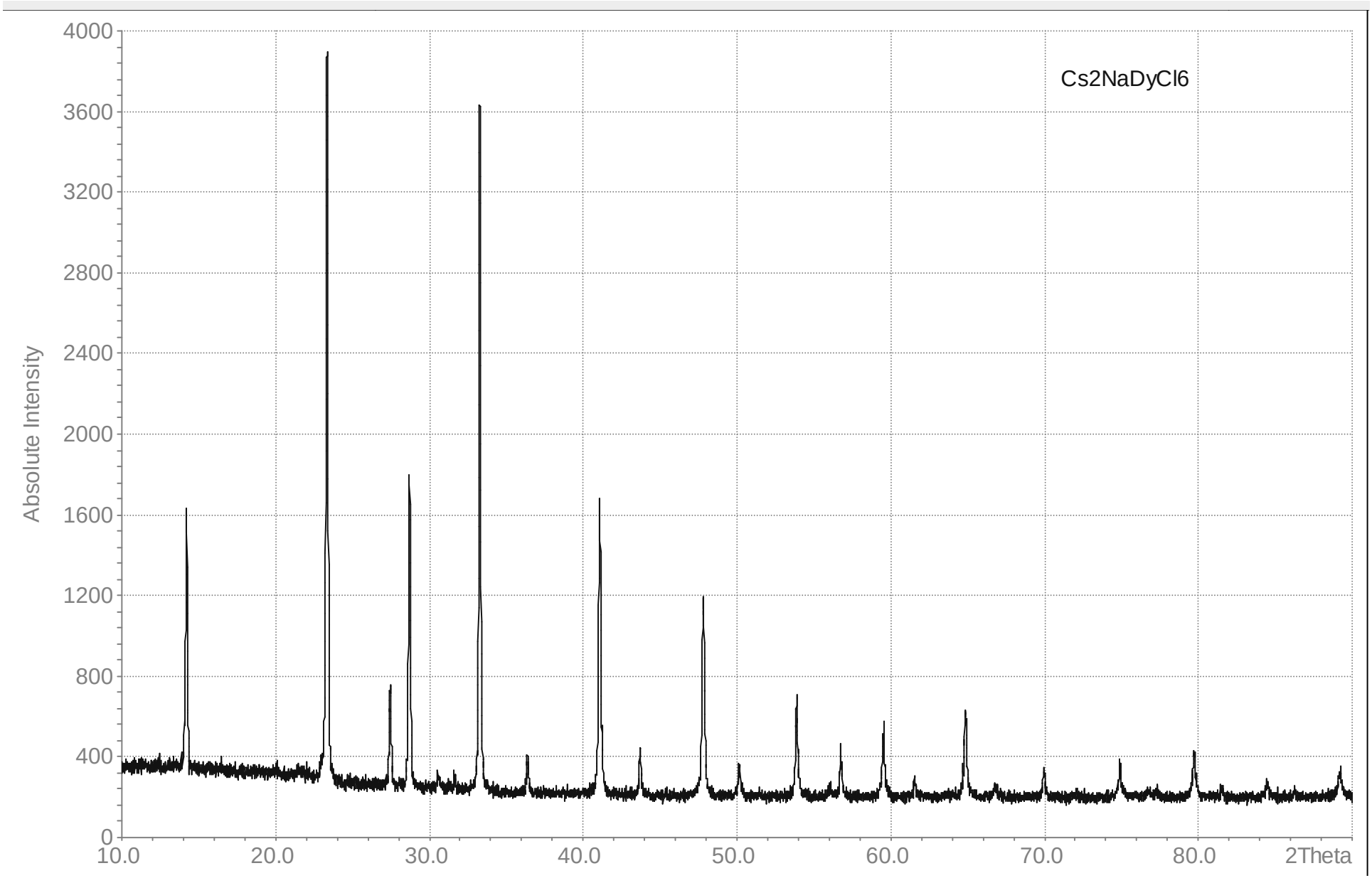
3. From single crystal to powder



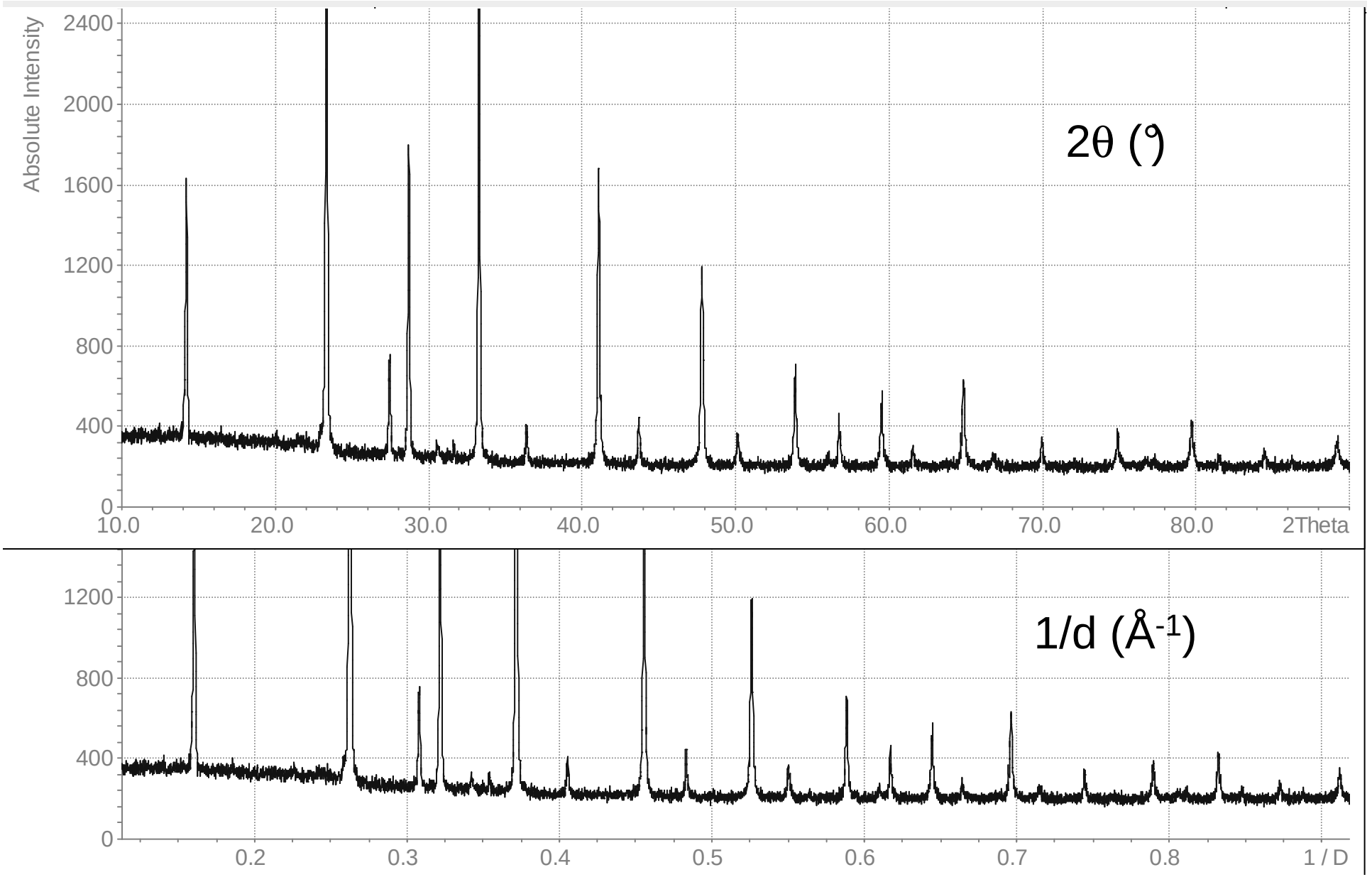
Information about crystal orientation is lost, i.e. the Miller index (hkl) of the reflection.

In powder
$\rightarrow$ only 2θ data.

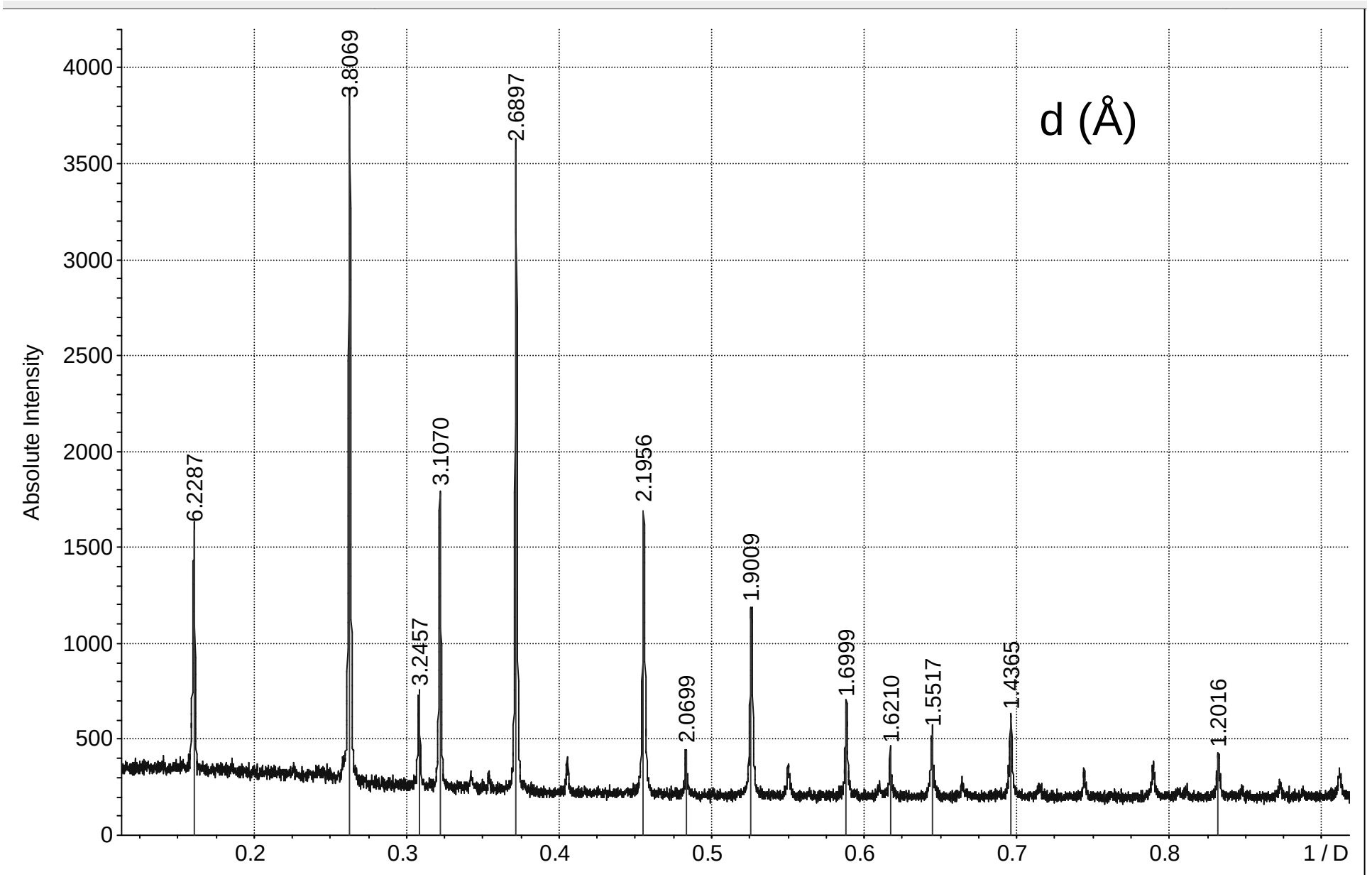
4. Powder diffraction



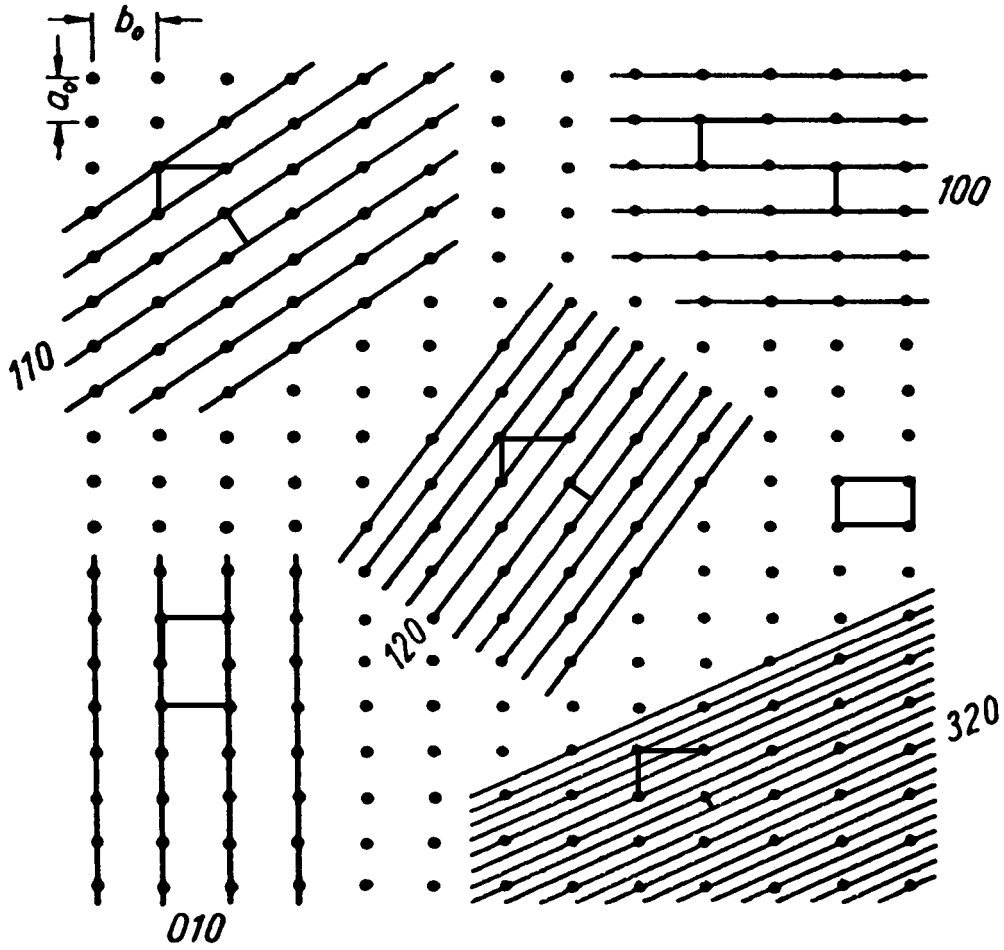
4. Powder diffraction



4. Powder diffraction



4. Diffraction (real space)



Miller‘s indices
hkl

layer distances
d

unit cell

large d-values $\rightarrow$ small 2θ-angles

sinθ ~ 1/d

4. The problem of powder indexing

$2\theta \rightarrow d \rightarrow a, b, c, \alpha, \beta, \gamma$ lattice parameters

$d \rightarrow h, k, l$ Miller‘s Indices

The reverse is simple.
Calculation of a theoretical pattern from crystal structure data
$2\theta \leftarrow d \leftarrow a, b, c, \alpha, \beta, \gamma$ lattice parameters

$I_{hkl} \leftarrow$ intensity calculation from space group and atomic positions

$\rightarrow$ Crystallography

4. The phase problem

$$I_{hkl} = PLG \cdot H \cdot A \cdot T \cdot |F_{hkl}^2|$$

PLG	polarisation, Lorentz, geometry factor
H	multiplicity (powder), for crystal H = 1
A	absorption factor
T	temperature factor, $T = e^{-(B \cdot \sin^2\theta / \lambda^2)}$
F	strukture factor

$$F_{hkl} = \Sigma_i f_i \cdot e^{2\pi i (h \cdot x_i + k \cdot y_i + l \cdot z_i)}$$

sum over all atoms i of the unit cell

f_i	atomic form factor (~ number of electrons)
x,y,z	atomic position

4. Powder versus single crystal diffraction

single crystal	determination of unknown (new) crystal structures
powder	analysis of phase and phase purity
	lattice parameter refinements
	crystal structure refinements of known structures (Rietveld method)
	structure solutions (very rarely)

Best data are obtained from

powder	for lattice parameters
crystals	for atomic parameters.

5. Crystallographic data

ICSD Inorganic crystal structure database (FIZ Karlsruhe)

CSD Cambridge structure database (organic compounds)

access via the web (license required)
$\rightarrow$ download a CIF file

(or use crystallographic data from literature)

crystallographic data
i) space group
ii) lattice parameters (positions of reflections 2θ)
iii) atomic positions (intensity of reflections I_{hkl})

$\rightarrow$ calculation of theoretical pattern

5. Crystallographic data

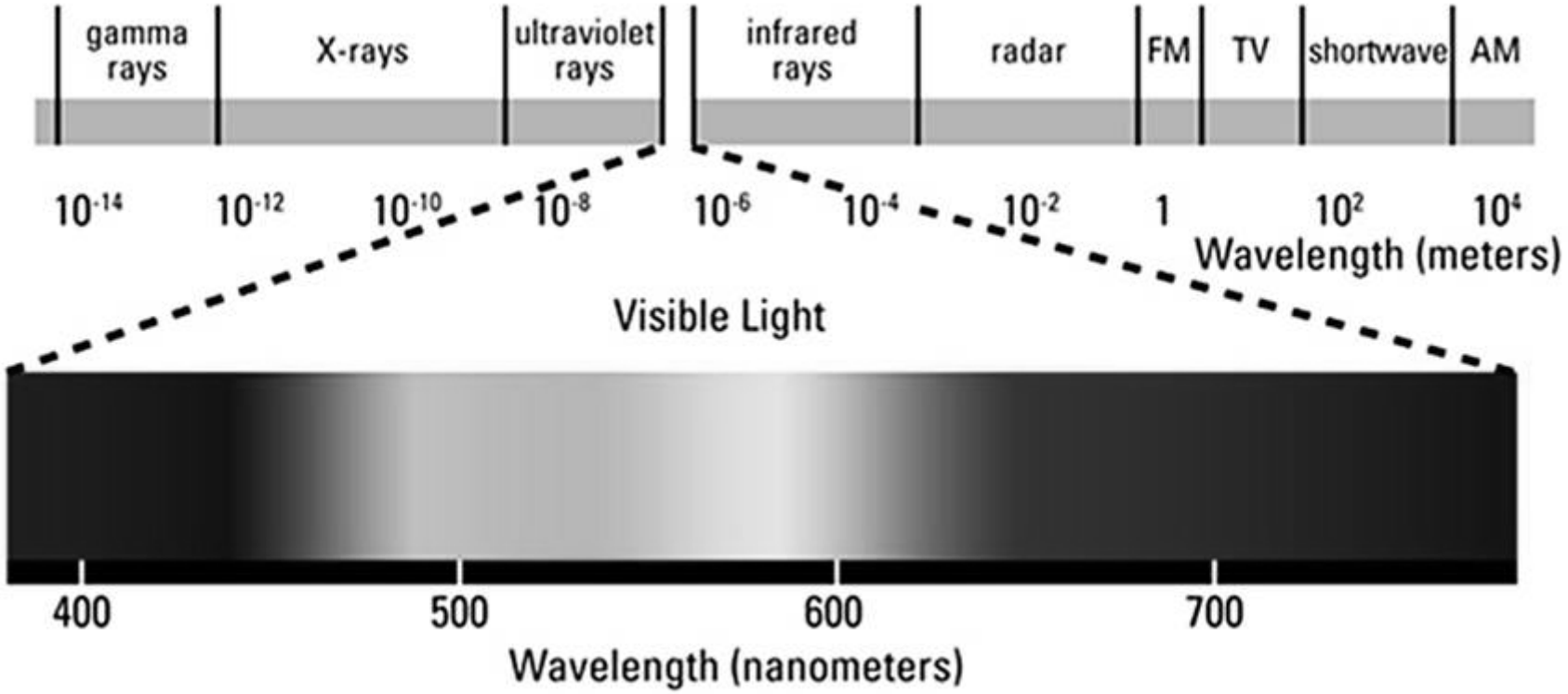
PDF Powder Diffraction File from ICDD (license required)
International Centre for diffraction data

Data base contains measured patterns
(be careful about → incomplete data (missing lines)
→ low quality data)

and

calculated patterns (from no. 65-xxxx onwards).

6. Electromagnetic radiation



← energy $E \sim \nu \sim 1/\lambda$

← ν

λ →

6. Electromagnetic radiation

wave → diffraction
photon → spectroscopy

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

$E \sim \nu \sim 1/\lambda$

$\lambda \nu = c$

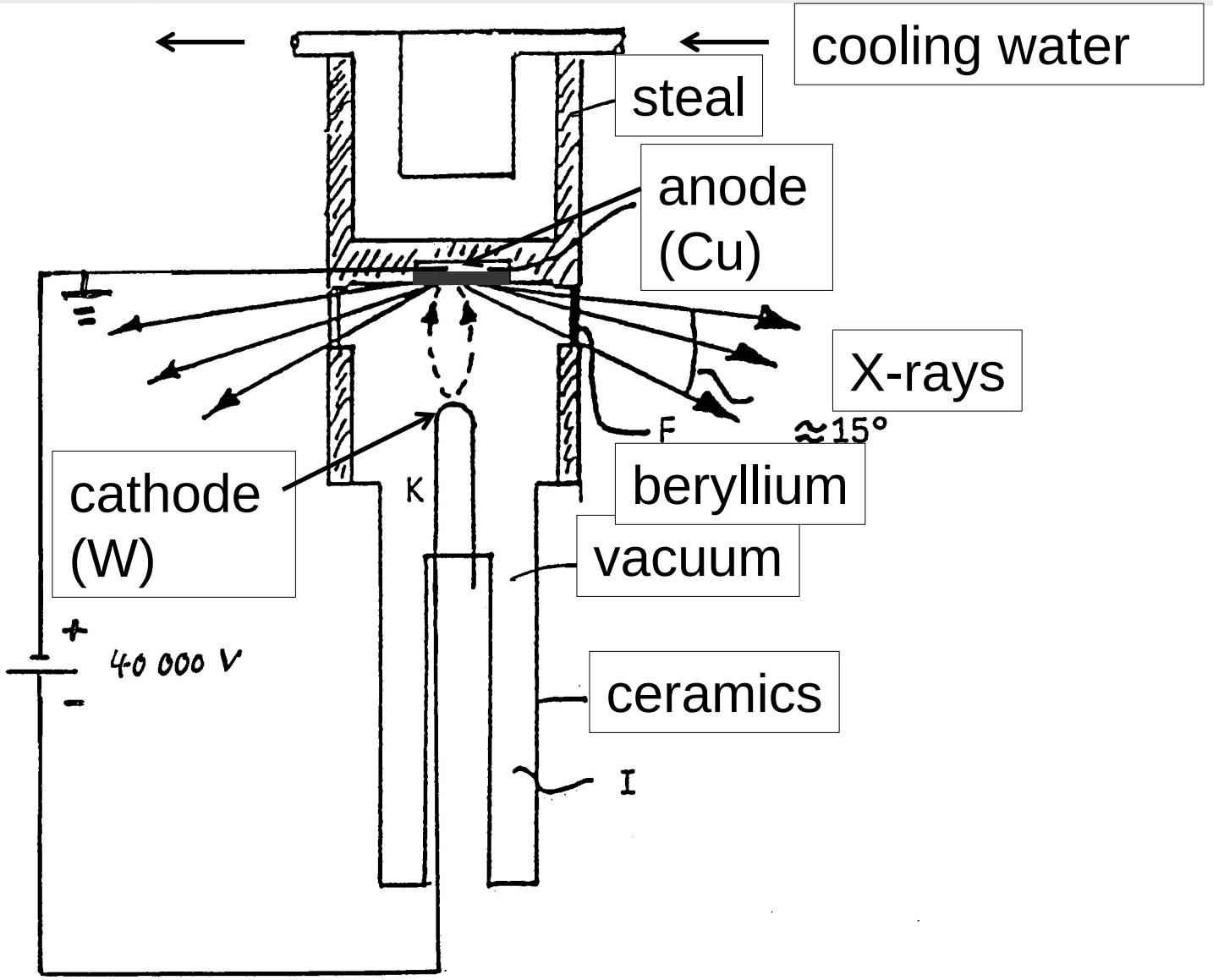
$h = 6{,}626 \cdot 10^{-34}$ Js — Planck's constant
$c_0 = 2{,}998 \cdot 10^{8}$ m/s — velocity of light in vacuum

ν frequency
λ wave length

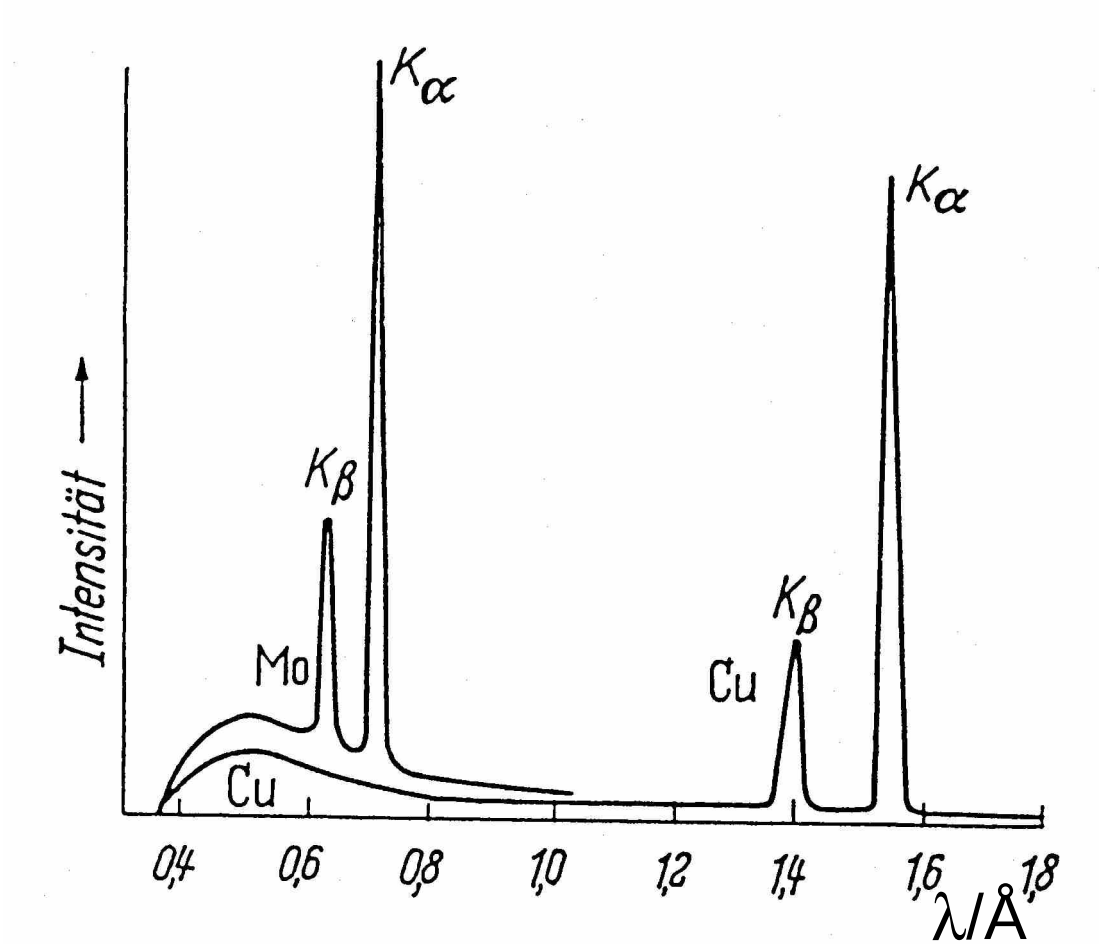
$\lambda(\text{Cu } K_\alpha) = 1.54$ Å
$\lambda(\text{Mo } K_\alpha) = 0.71$ Å

1 Å $= 10^{-10}$ m

6.1. X-ray tube


cooling water
steal
anode
(Cu)
X-rays
≈15°
F
cathode
(W)
K
beryllium
vacuum
+
40 000 V
−
ceramics
I

6.1. X-rays from an X-ray tube



characteristic radiation
→ anode material

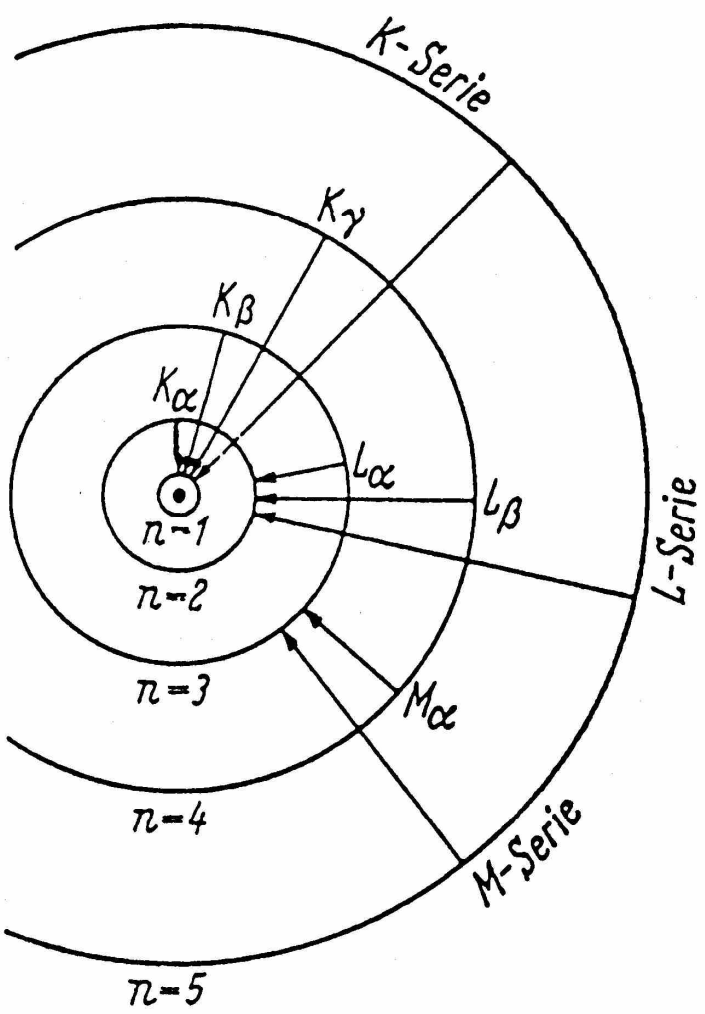
Cu Kα 1.54 Å

Mo Kα 0.71 Å

continuous spectrum (Bremsstrahlung)

$\lambda_{min.} \rightarrow$ kinetic energy of electron, $E_{max.} = U\ e$

6.2. Characteristic radiation



Moseley‘s law

$E = A\,(Z - \sigma)^2\,(1/n_1^2 - 1/n_2^2)$

A constant
Z atomic number
(= nucleus charge)
σ shielding constant
n_1, n_2 quantum numbers

K-series $\rightarrow n_1=1$
α $\rightarrow \Delta n=1$

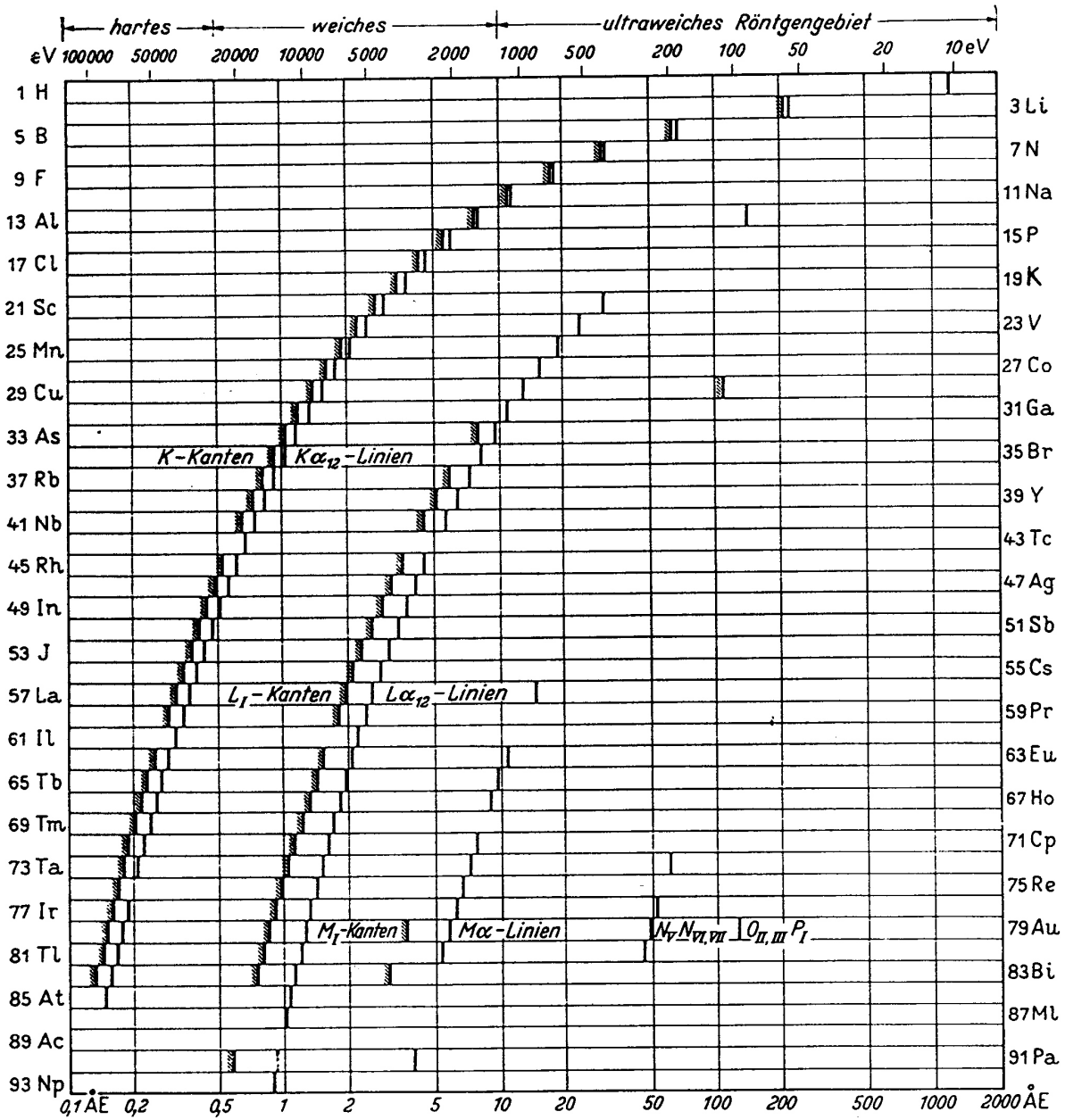


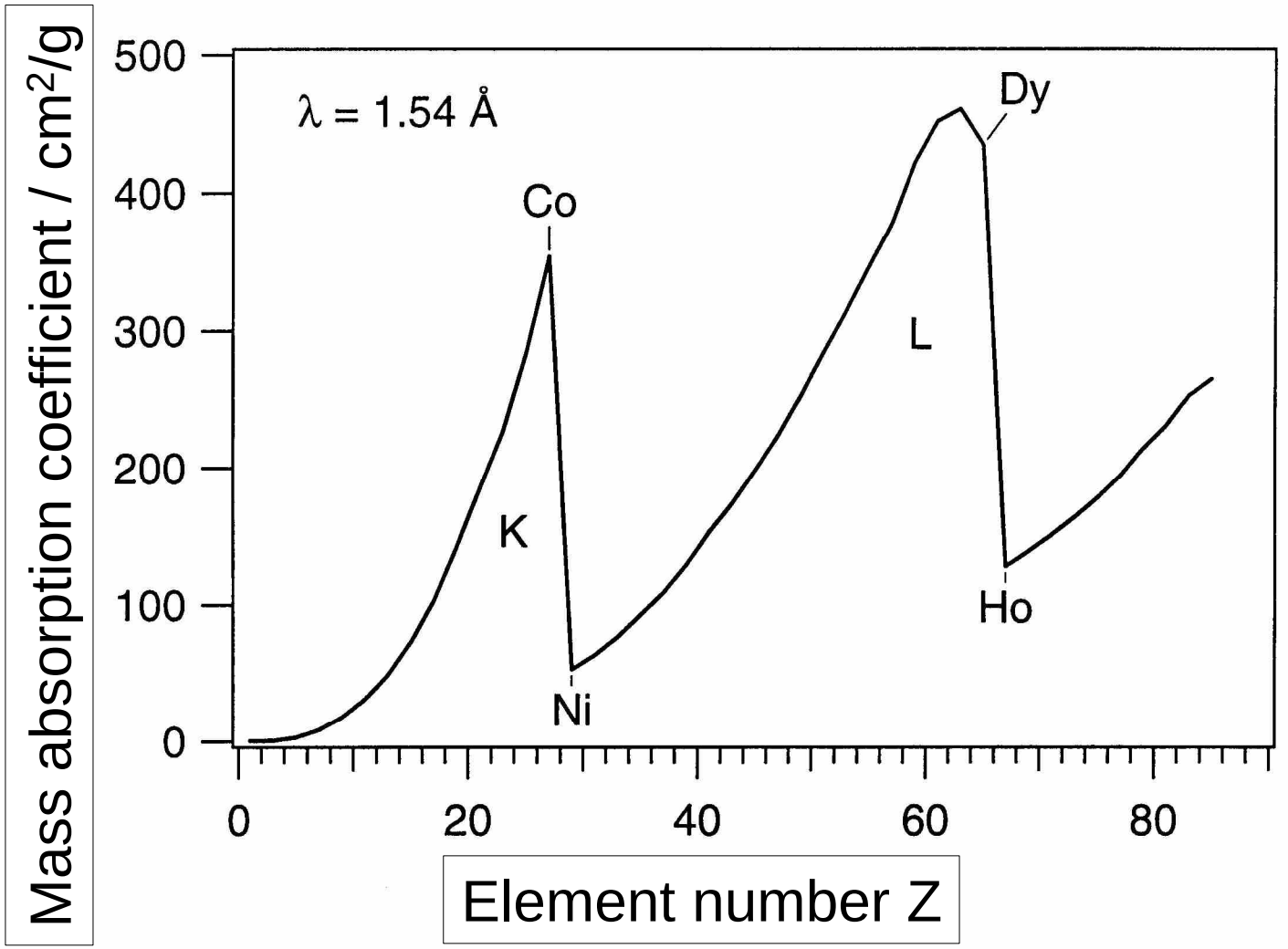
Abb. 4. Übersicht über die Lage der wichtigsten Absorptionskanten und Emissionslinien der Elemente mit ungeraden Ordnungszahlen. (Entn.: LANDOLT-BÖRNSTEIN: 1. Teil, 6. Aufl. Berlin/ Göttingen/Heidelberg: Springer 1950)

characteristic radiation

Kα

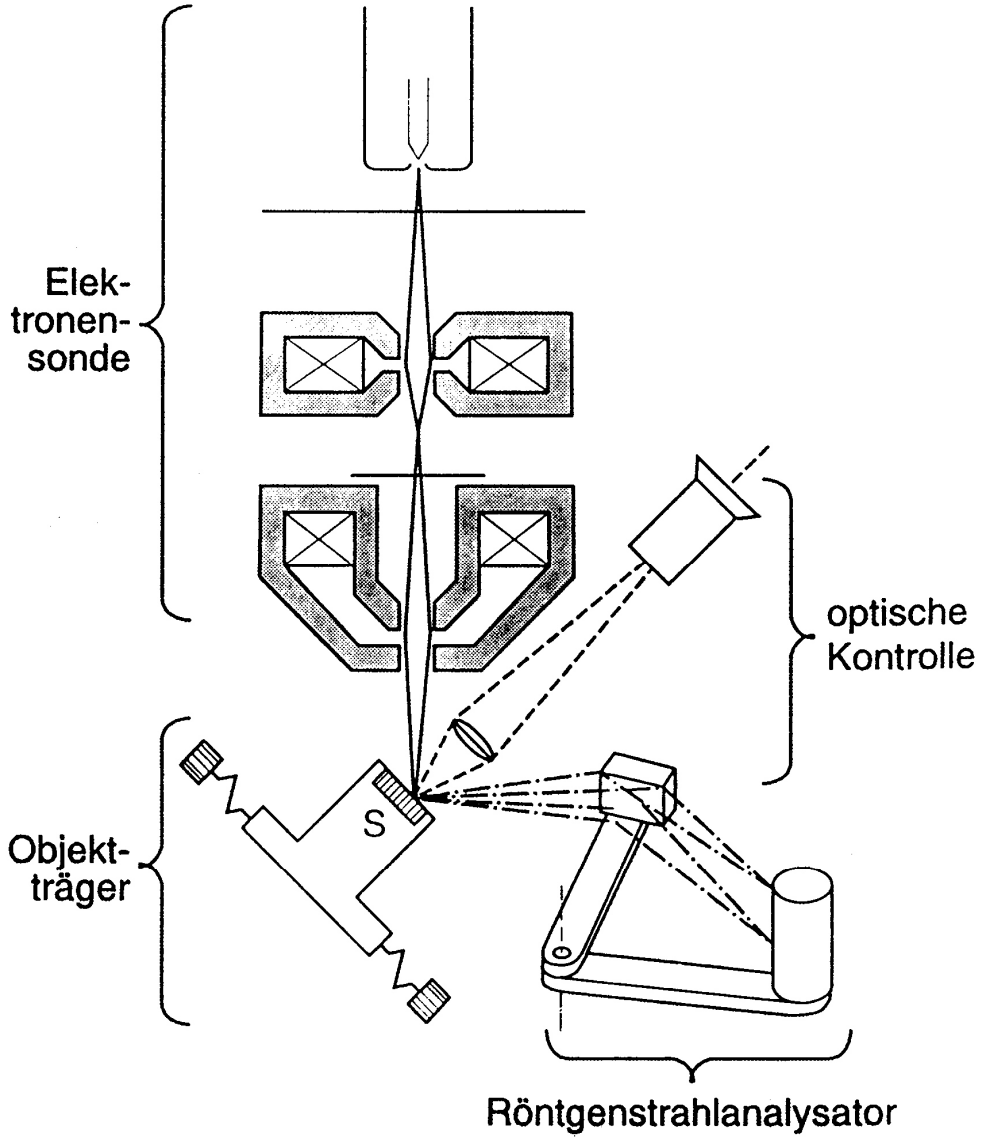
$E \sim (Z - 1)^2$

6.2. Absorption of Cu Kα radiation



The K-line of element Z is strongly absorbed by element Z-2.

7. Element analysis by EDS in a SEM



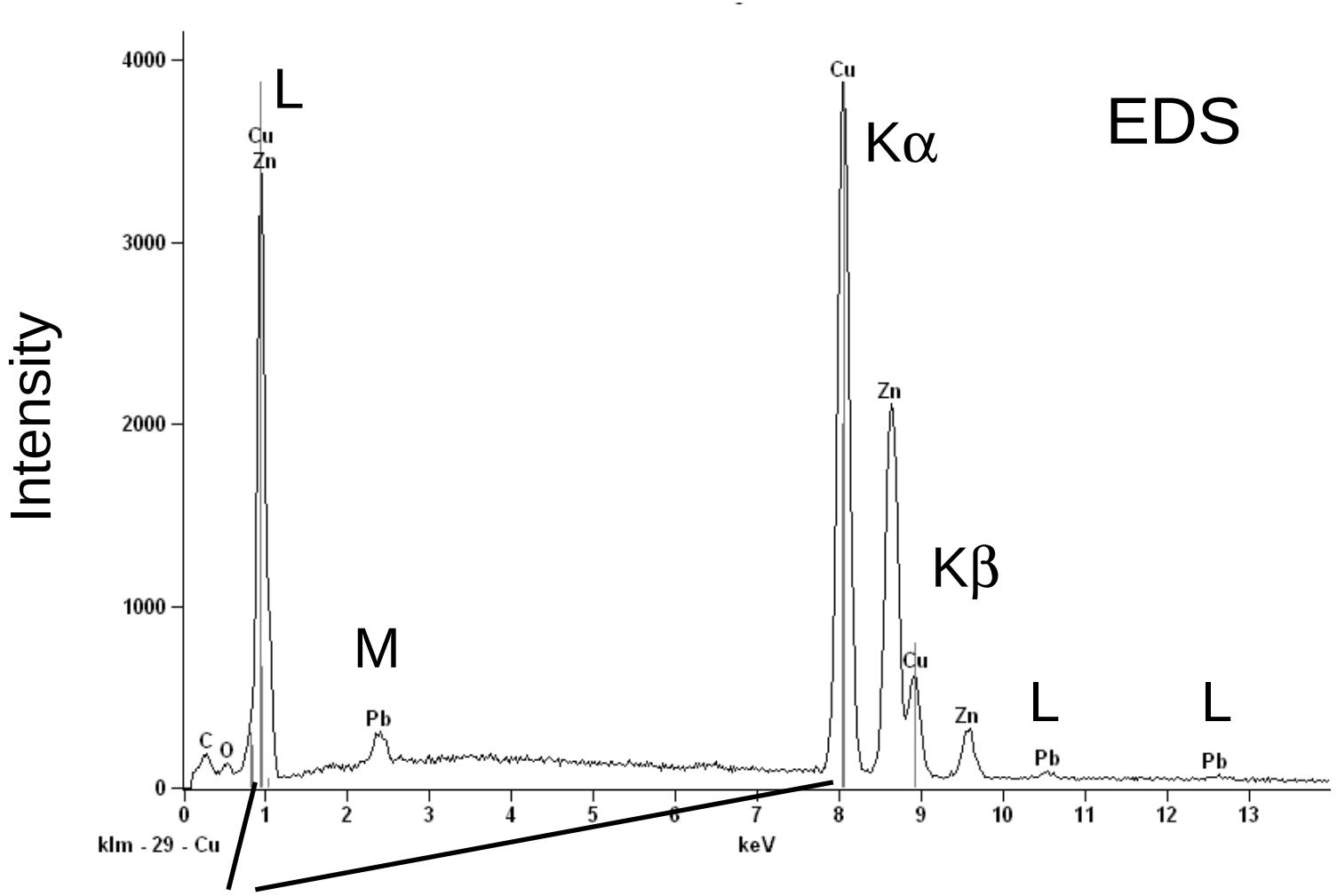
Energy dispersive X-ray spectrometry (EDS)

The electron beam ionizes atoms in the sample (S).
The atoms emit characteristic X-rays.

wave length (energy)
→ element

intensity
→ composition

7. Element analysis by EDS in a SEM



brass
main constituents: Cu, Zn
minor constituent: Pb

7. Element analysis by EDS in a SEM

Element Line	*Weight %*	*Weight % Error*	*Atom %*	*Atom % Error*
Cu K	59.60	+/- 0.45	61.89	+/- 0.47
Zn K	36.53	+/- 0.49	36.88	+/- 0.49
Pb L	3.87	+/- 0.48	1.23	+/- 0.15
Total	100.00		100.00	

wave length (energy) $\rightarrow$ element

intensity $\rightarrow$ composition