

Lecture: Solid State Chemistry - WP I/II

Chapter 4: Physical methods in Solid State Chemistry

- 4.1 Electromagnetic radiation
- 4.2 Microscopic techniques: OM, SEM, CTEM, HREM
- 4.3 X-ray diffraction: XRD, XRPD
- 4.4 Photoelectron spectroscopy: ESCA
- 4.5 X-ray absorption spectroscopy: EXAFS, XANES
- 4.6 Moessbauer spectroscopy
- 4.7 Impedance spectroscopy (ionic conductivity)
- 4.8 Magnetic measurements
- 4.9 Thermal analysis: TA, DTA, DSC, TG
- 4.10 Comparison of some techniques for structural studies

4. Physical methods in Solid State Chemistry

Physical methods in Solid State Chemistry must/should/can be sensitive with respect to the:

- Composition of a compound/molecule
- States/energies of spins, electrons, rotations, vibrations, atoms/molecules etc.
- States/energies of compounds/reactions
- Sites/positions of the atoms/ions/molecules etc.
- Extension etc.

Resulting in microscopic, spectroscopic, thermal, ... methods/techniques.

Most of the methods use electromagnetic radiation.

4.1 Electromagnetic Radiation: Characteristics

transversal waves, velocity $c_0 \approx 3 \cdot 10^8 \text{ m s}^{-1}$

1. Energy (eV, kJ mol⁻¹)

-frequency ν ($\nu = c_0 / \lambda$; s⁻¹, Hz)

-wavelength λ ($\lambda = c_0 / \nu$; Å, nm, ..., m, ...)

-wavenumber $\tilde{\nu}$ ($\tilde{\nu} = 1/\lambda = \nu/c_0$; cm⁻¹, Kaiser)

energy $\sim$ frequency ($E = h \cdot \nu$)

$\sim$ wavenumber ($E = h \cdot \tilde{\nu} \cdot c_0$)

$\sim$ wavelength⁻¹ ($E = h \cdot c_0 / \lambda$)

2. Intensity

cross-section $I \sim |\vec{S}|^2 = |\vec{E} \times \vec{H}|$

3. Direction

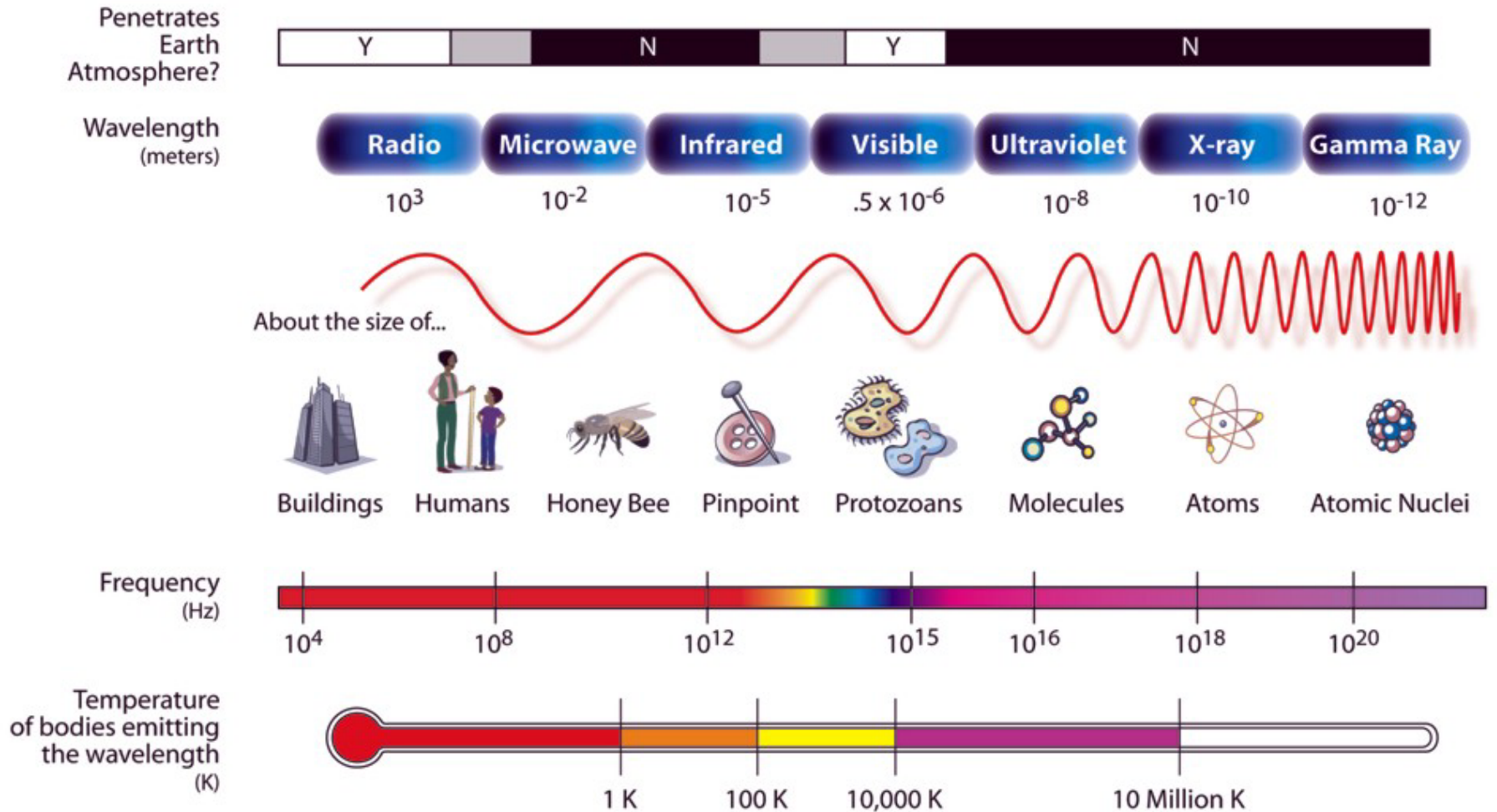
wavevector $\vec{S}_0$

4. Phase

phase φ

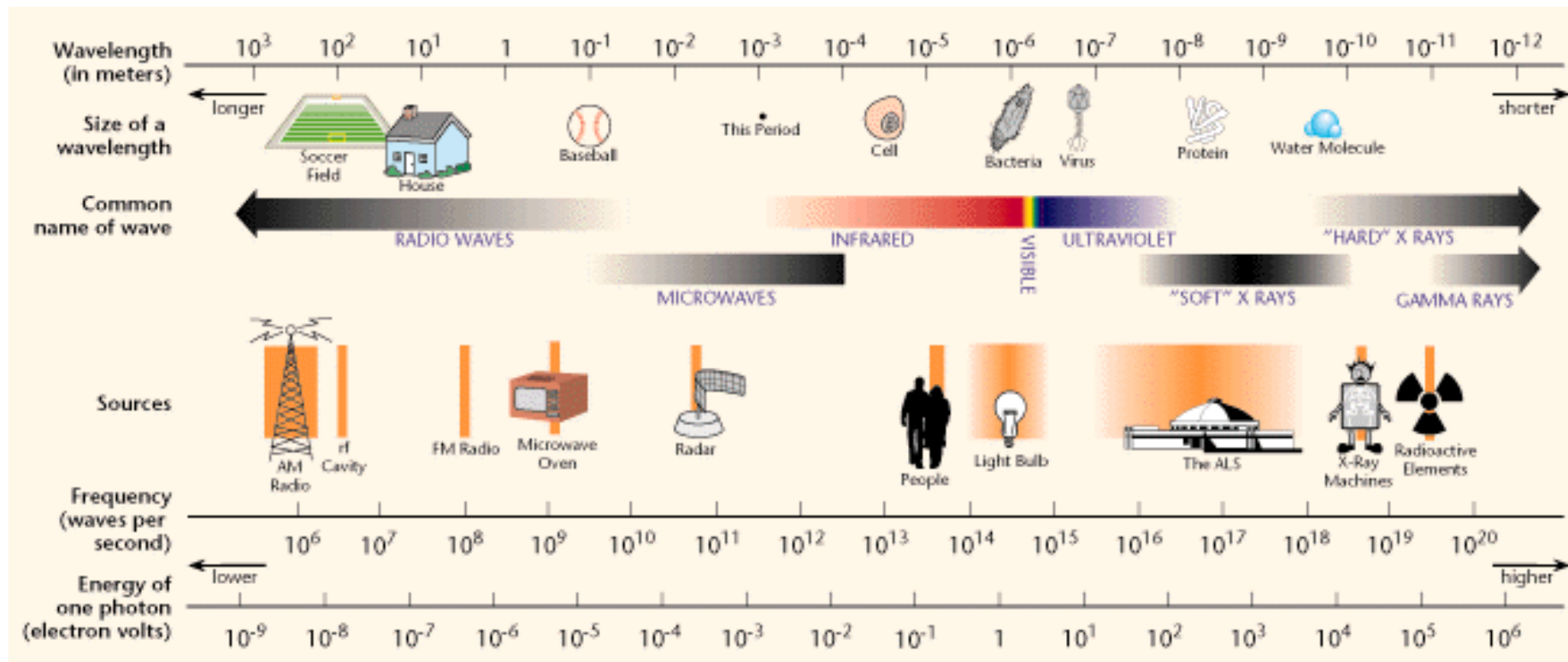
Range of frequencies for structural analysis: 10⁶-10²⁰ Hz, 10² -10⁻¹²m, 10⁻⁸-10⁶ eV
radio-, microwaves, infrared (IR), visible (VIS), ultraviolet (UV), X-ray, γ -ray³

4.1 Electromagnetic radiation: Spectral ranges



Orders of magnitude in wavelength, frequency, energy, temperature

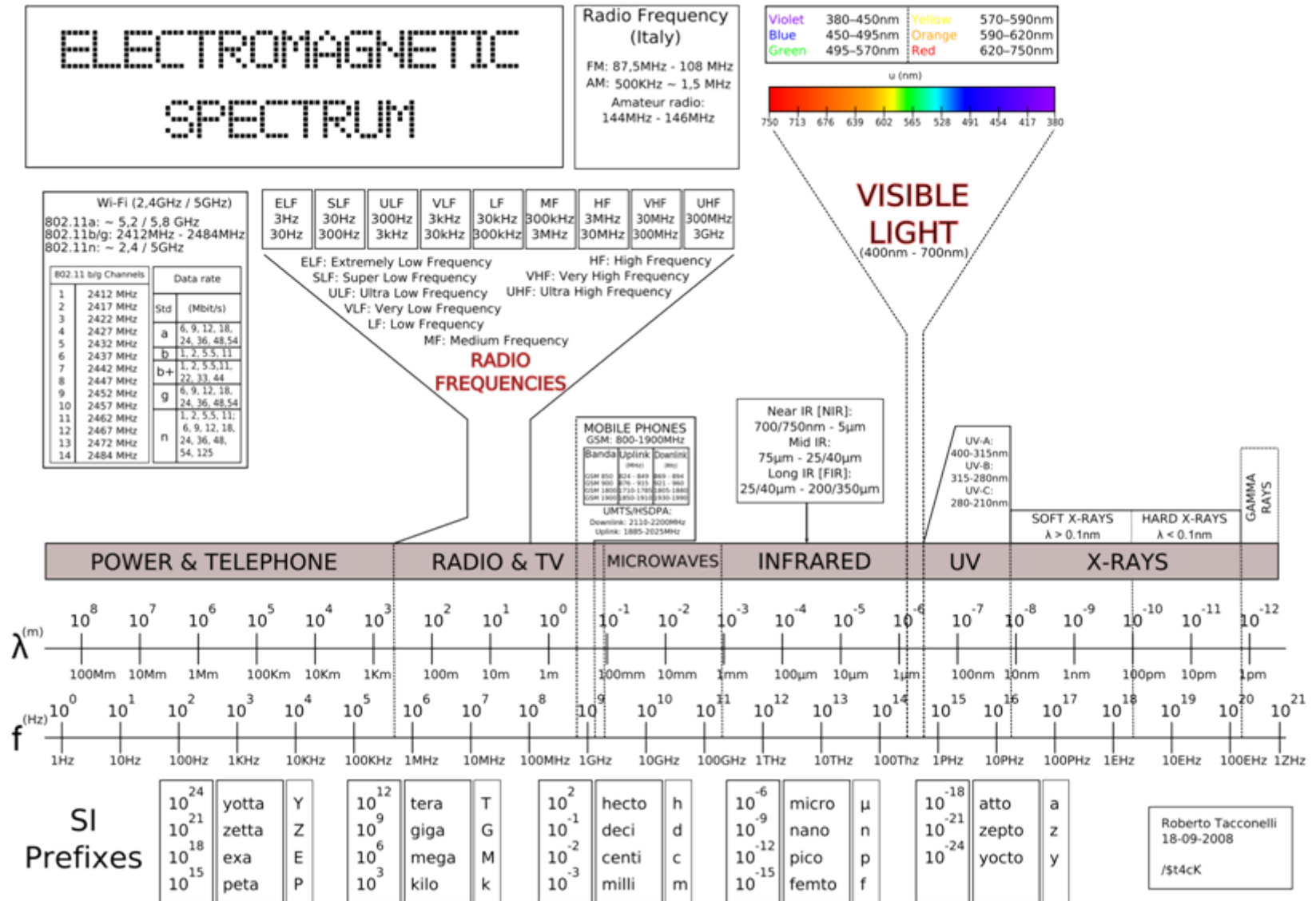
4.1 Electromagnetic radiation: Spectral ranges



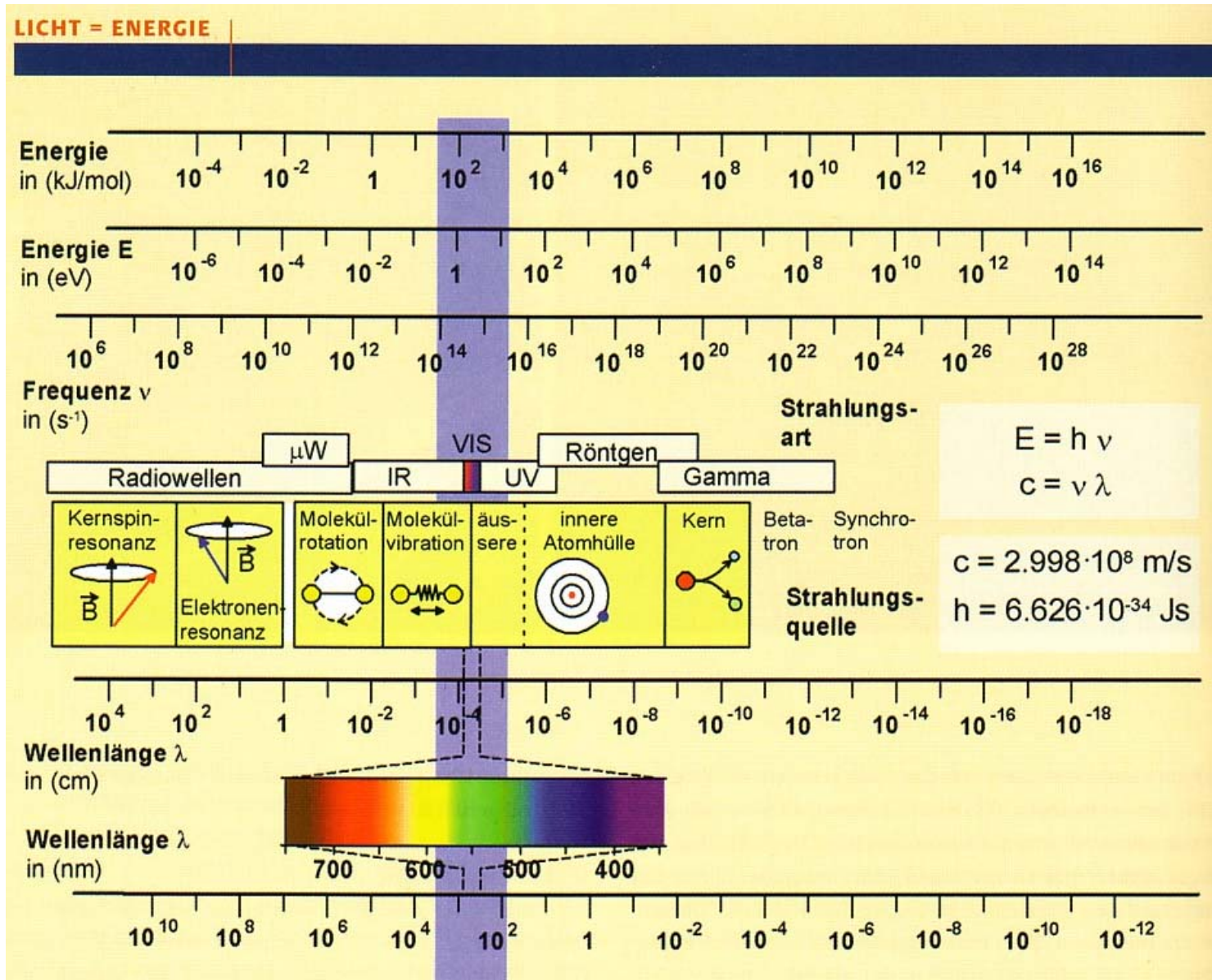
$$1 \text{ eV} = 1,602 \cdot 10^{-19} \text{ J} = 96,485 \text{ kJ mol}^{-1} = 8065,5 \text{ cm}^{-1}$$

Orders of magnitude in wavelength, frequency, energy, temperature

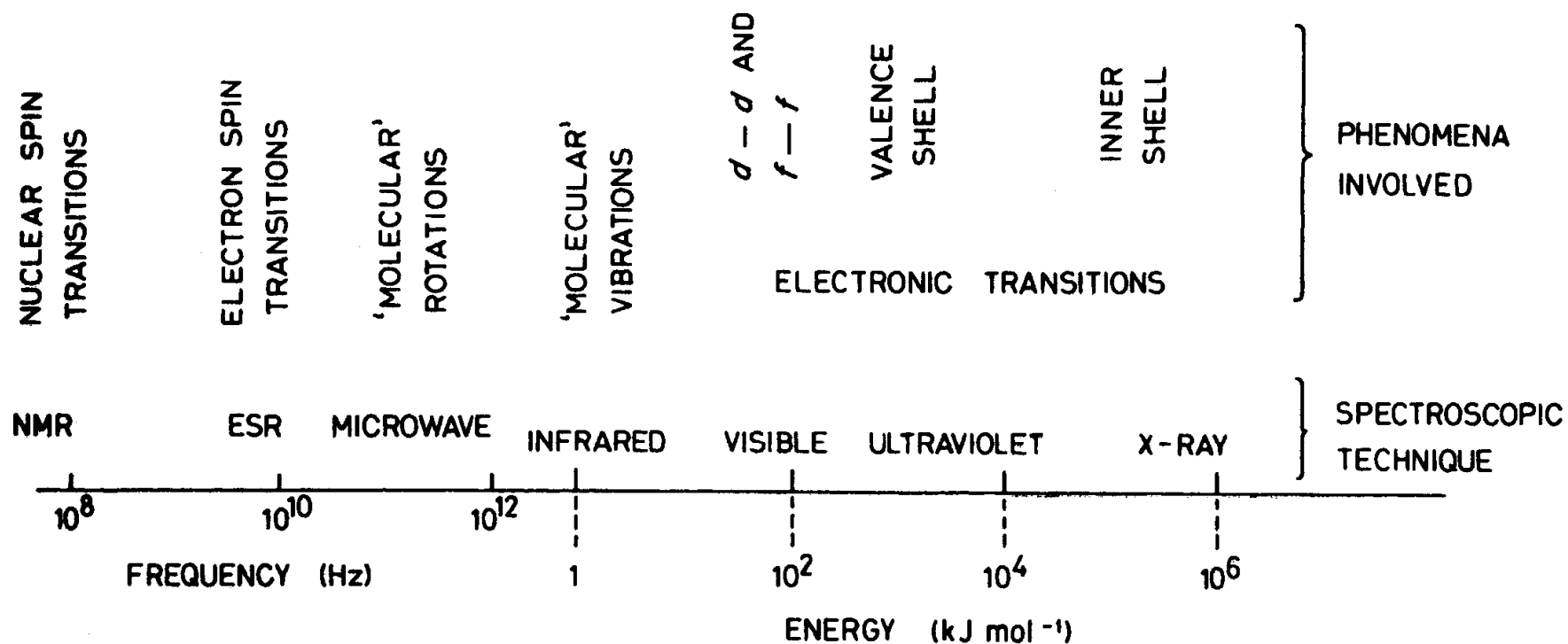
4.1 Electromagnetic radiation: Spectral ranges



4.1 Electromagnetic radiation: Spectral ranges



4.1 Electromagnetic radiation: Origins and techniques



4.1 Electromagnetic radiation: Sources

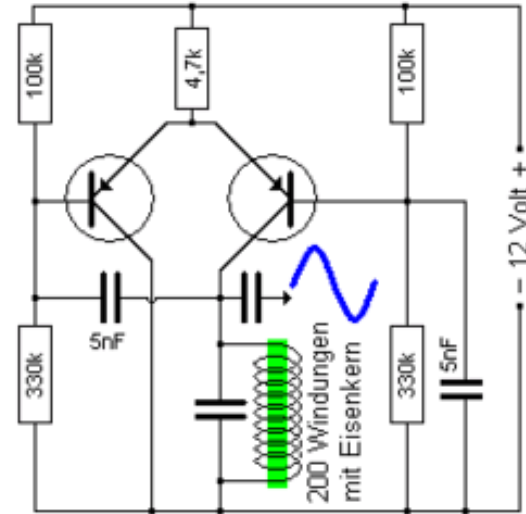
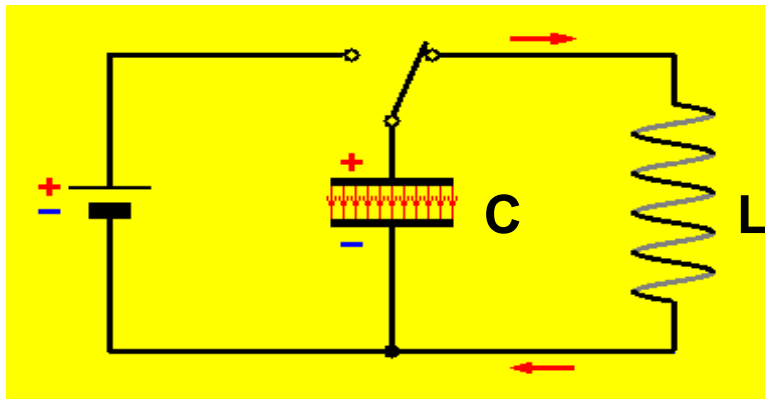
Radio waves/NMR



Radio valve, 500 W
graphite anode



Anode



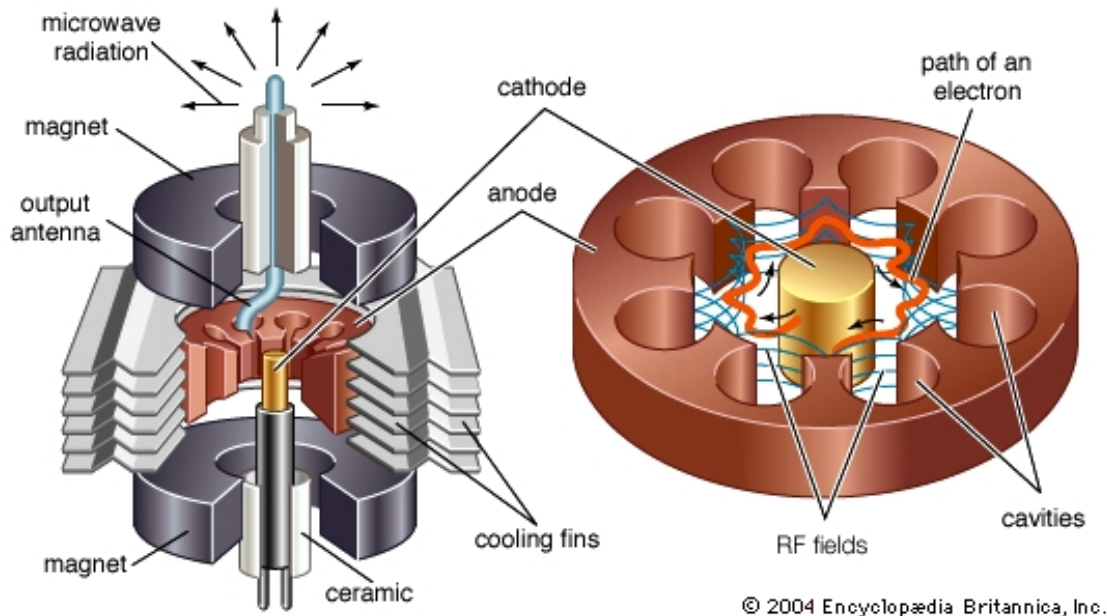
Sinus-Oszillator für etwa 1 kHz mit PNP-Transistoren.

$$f = \frac{1}{2\pi} \sqrt{\frac{1}{LC}}$$

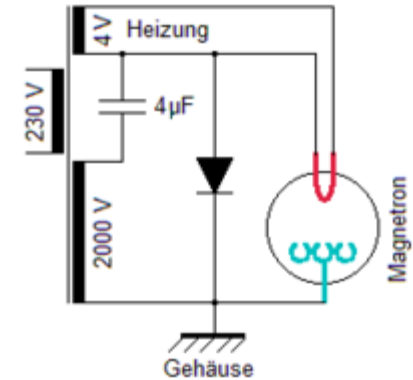
Electromagnetic waves are produced (a.o.), when charges or charged or dipolar species are oscillating with frequencies in the respective range. For microwaves, the charges oscillate in a resonance or tank circuit, consisting of a capacitor with capacitance C and a coil with self-inductance L .

4.1 Electromagnetic radiation: Sources

Microwave radiation



Schematic view of a magnetron for the production of microwaves (left) and the anode with an even number of anode vanes (right)



Principal circuit of a magnetron



Impulsmagnetron MI-189W (ca. 9 GHz)
Bordradar, Russia

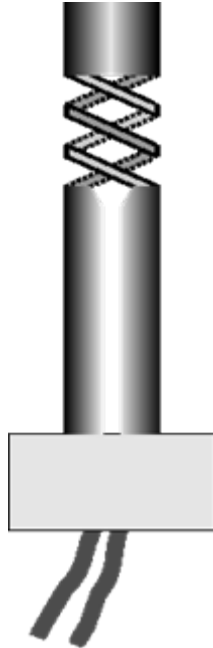
Magnetrons and Gyrotrons are diode-type electron tubes ($\sim 1\text{-}10\text{ kV}$) with a trapezoid anode (*resonant cavities*) surrounded by permanent magnets producing an axial magnetic field. Under the combined influence of the electric and the magnetic field, the electrons are forced in a circular motion of travel to the anode resulting in electromagnetic radiation of $0.3 - 300\text{ GHz}$.

4.1 Electromagnetic radiation: Sources

IR-Sources, Globar, Nernst lamp



new

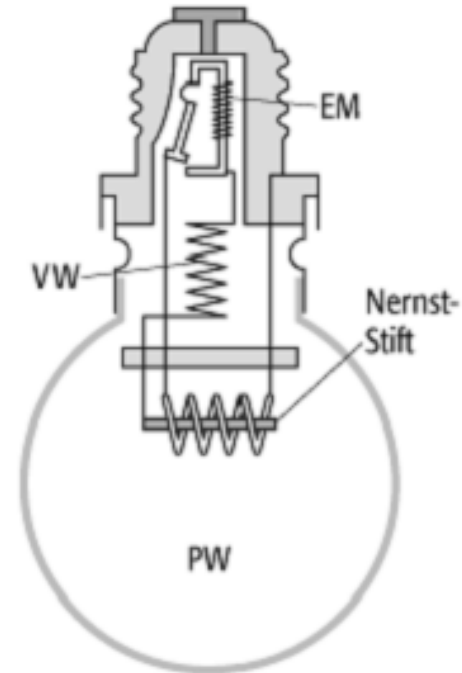


sketch



used

Globar (SiC, ~1.500 K)

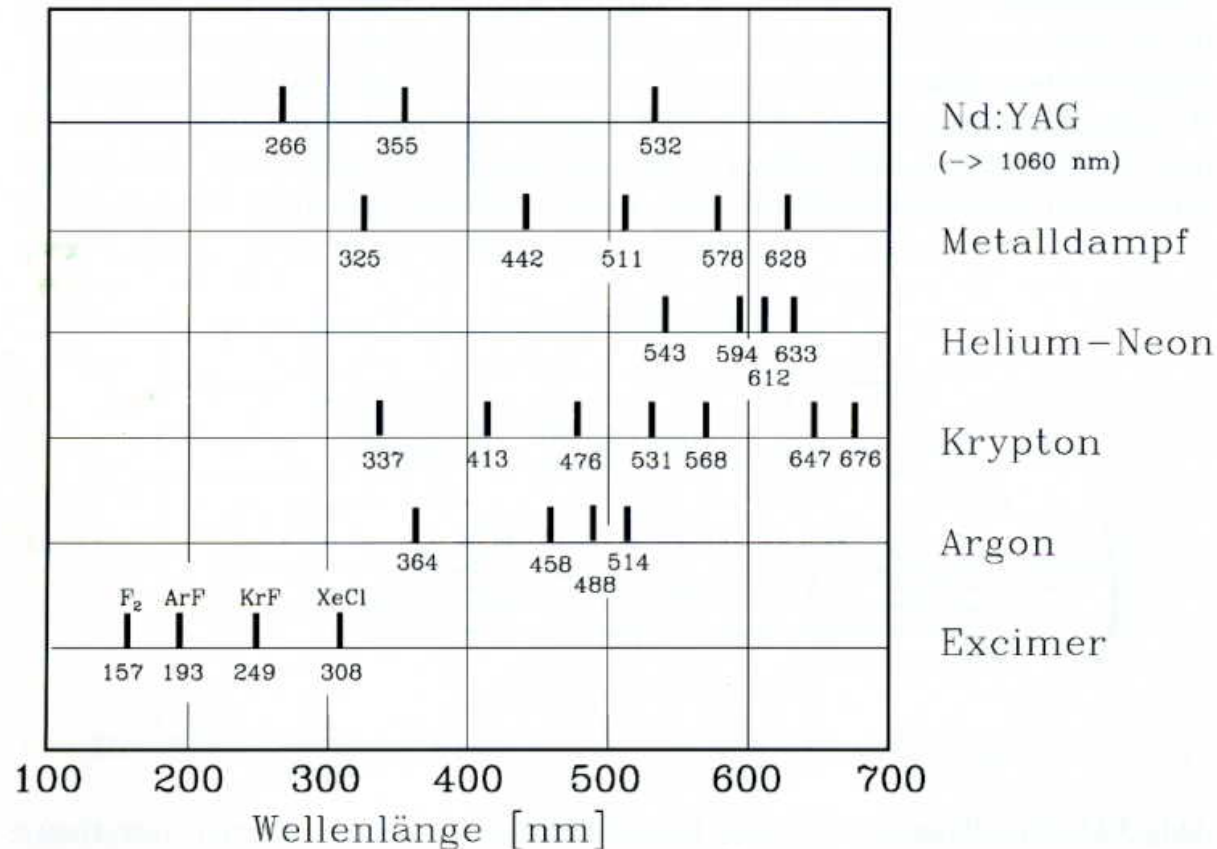


Nernst lamp with Nernst rod, a
 $\text{ZrO}_2/\text{Y}_2\text{O}_3$ ion conductor 1.900 K

Any heated material will produce infrared radiations

4.1 Electromagnetic radiation: Sources

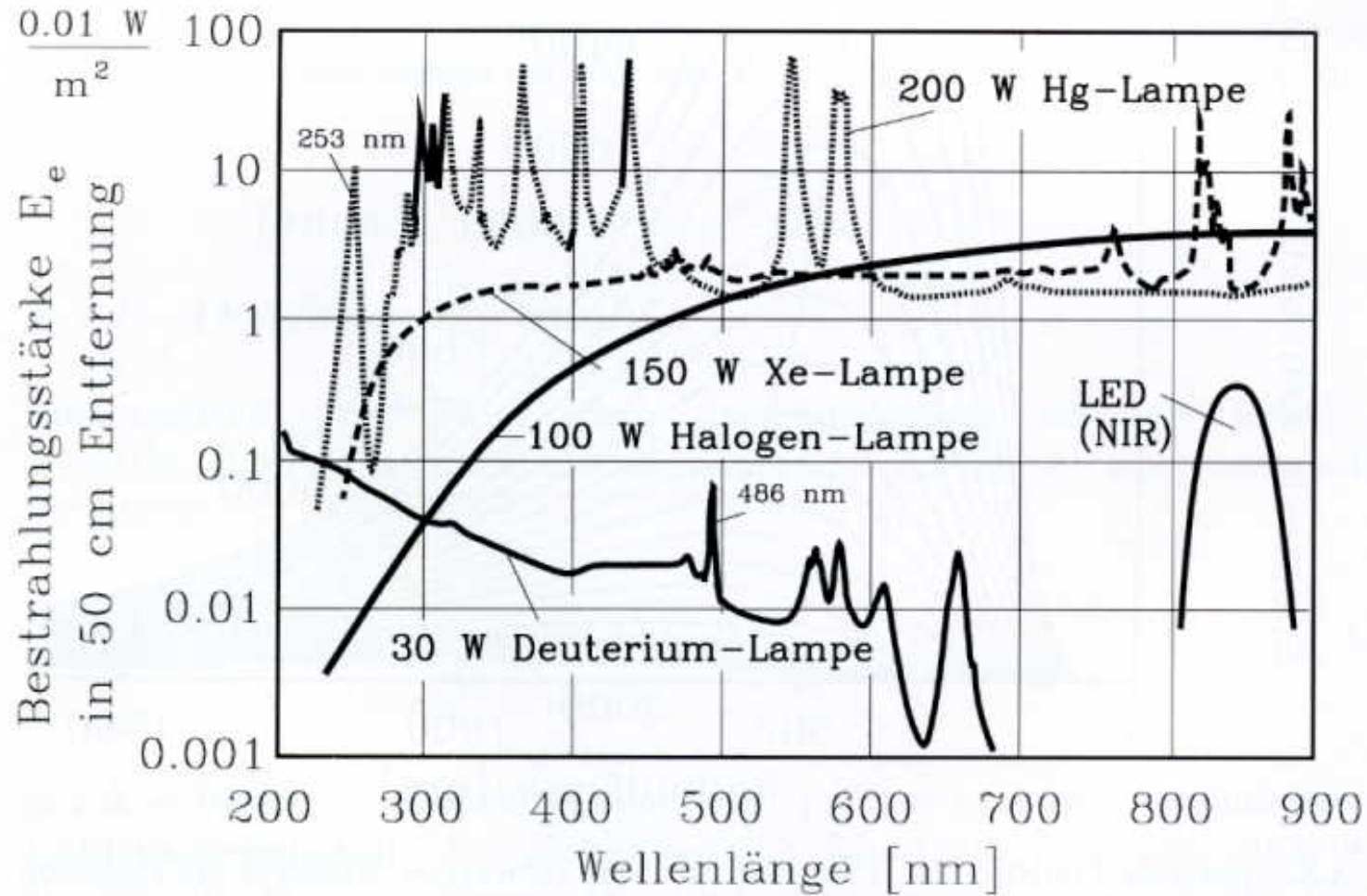
UV and NIR radiation



Wave lengths of some lasers for UV, visible and Raman spectroscopy

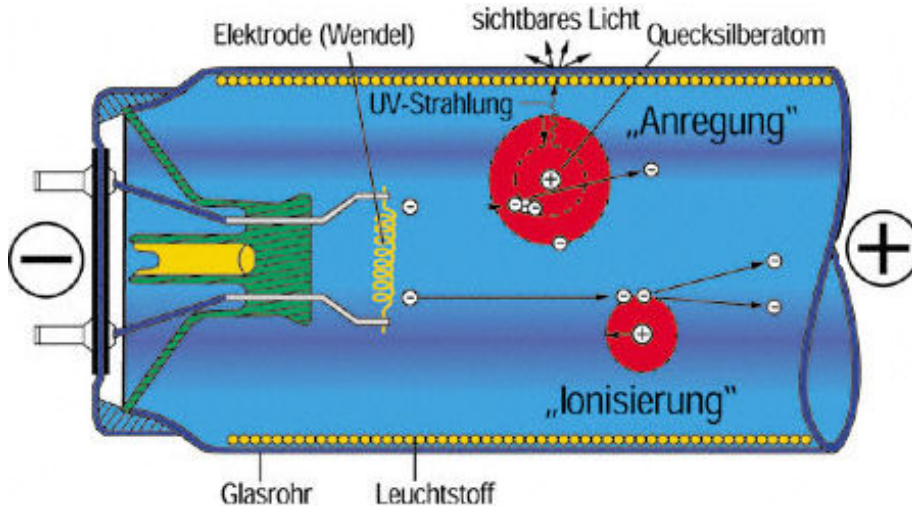
4.1 Electromagnetic radiation: Sources

UV and NIR radiation



4.1 Electromagnetic radiation: Sources

UV radiation



Sketch of a mercury (low pressure) lamp
Excitation/ionisation of Hg by fast electrons
(Important Hg lines are 313 nm, 365 nm (i line),
405 nm (h line), 434 nm (g line), 546 nm (e line) and
577/579 nm und nm (orange dubble line)).



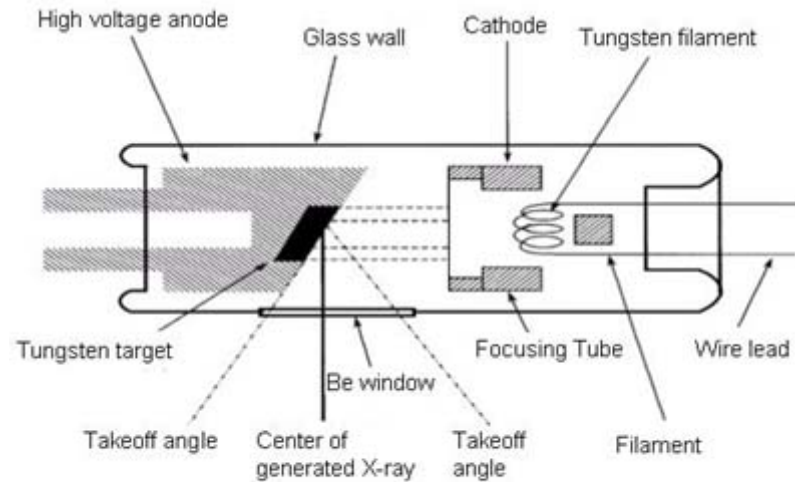
UV or black light lamp

4.1 Electromagnetic radiation: Sources

X-rays



X-rax tube



X-rax tube: sketched and dashed

4.1 Electromagnetic radiation: Sources

Synchrotron

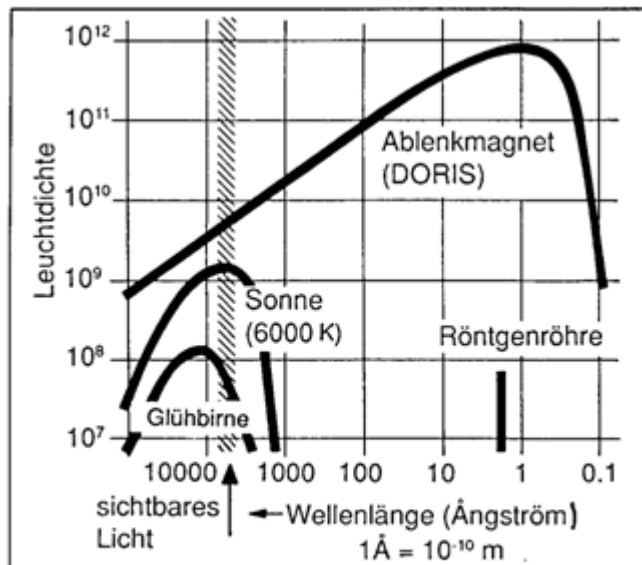
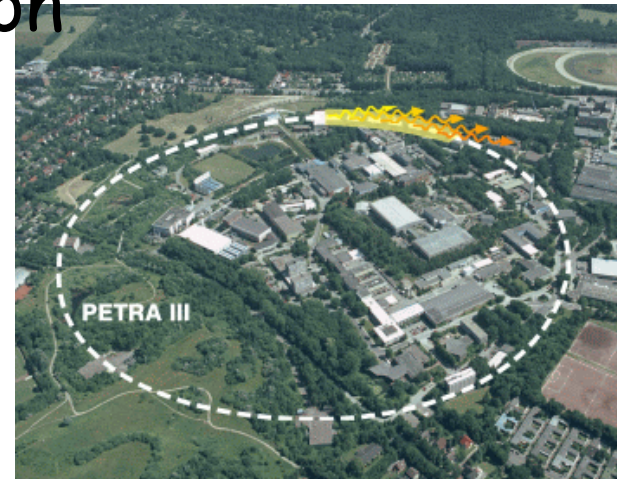
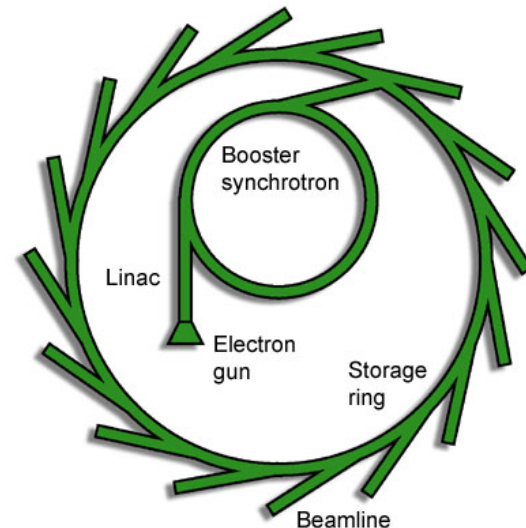


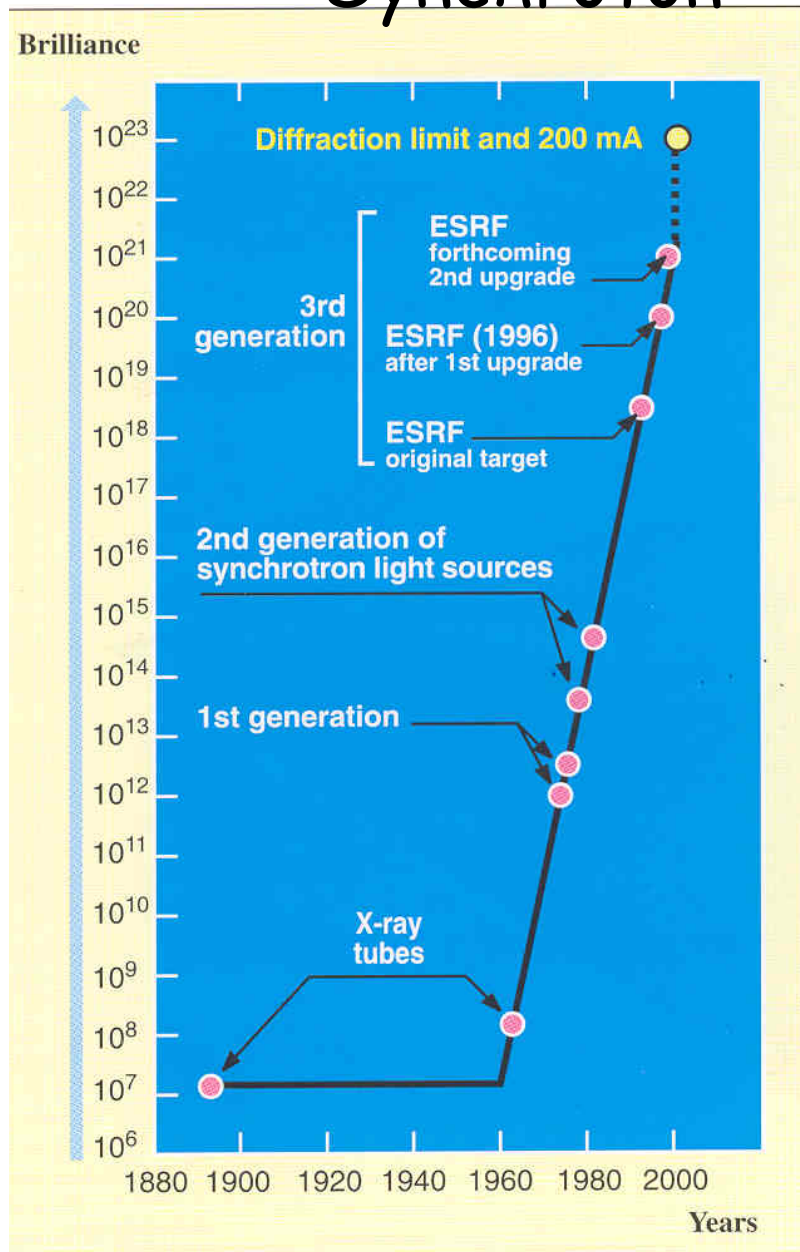
Abb. 5: Die Leuchtdichte von DORIS im Vergleich zu einigen bekannten Strahlungsquellen. (Die Leuchtdichte ist die Zahl der Photonen, die pro Sekunde und Wellenlängenintervall in eine bestimmte Richtung abgestrahlt wird.)



tunable electromagnetic radiation

4.1 Electromagnetic radiation: Sources

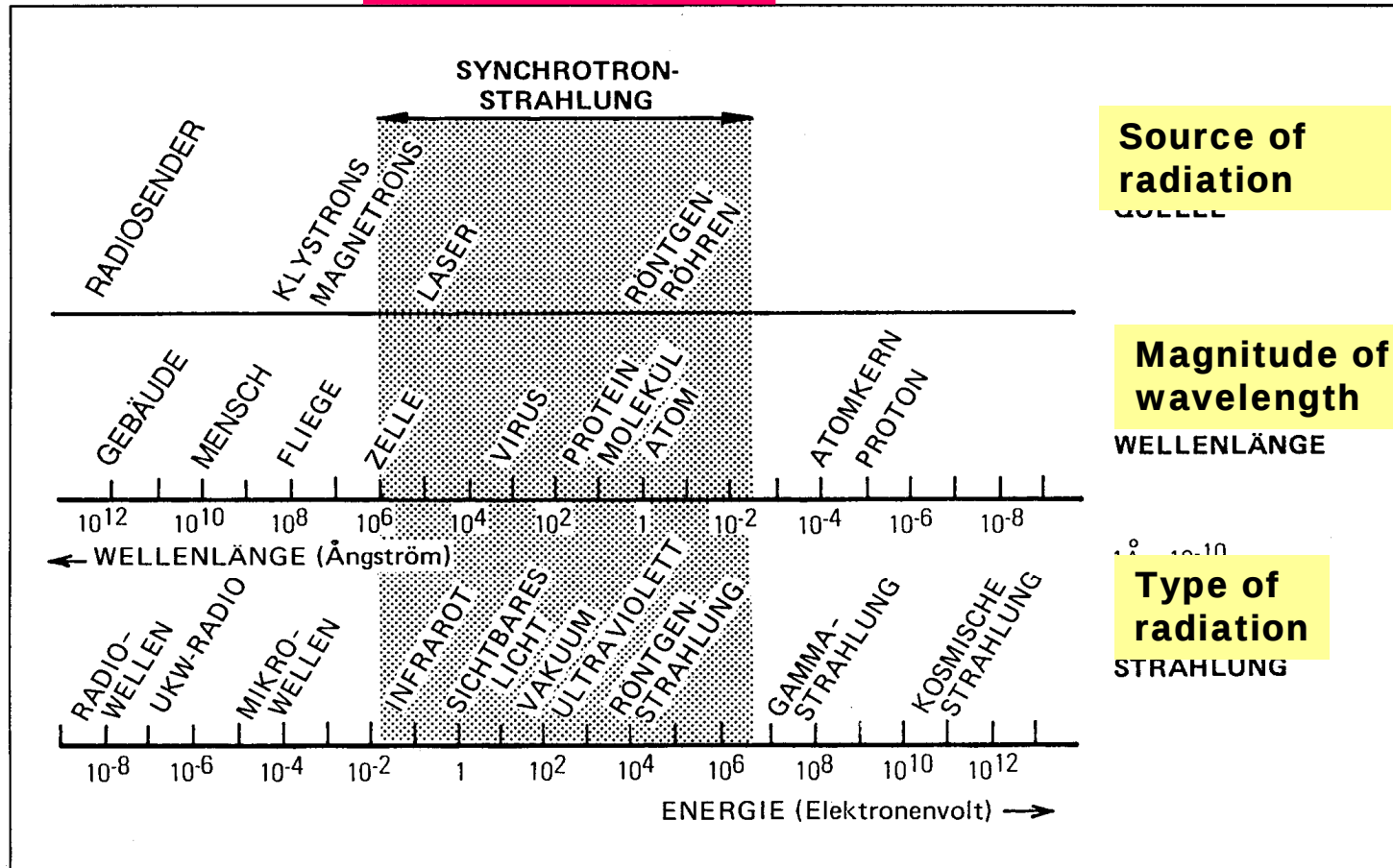
Synchrotron



increase of
brilliance over the
years

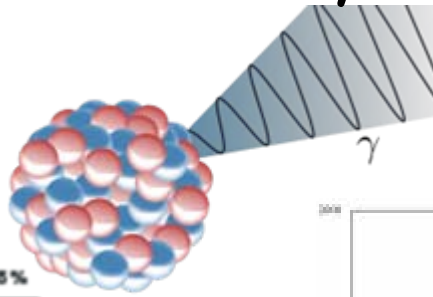
4.1 Electromagnetic radiation: Sources Synchrotron

(range of tunability)

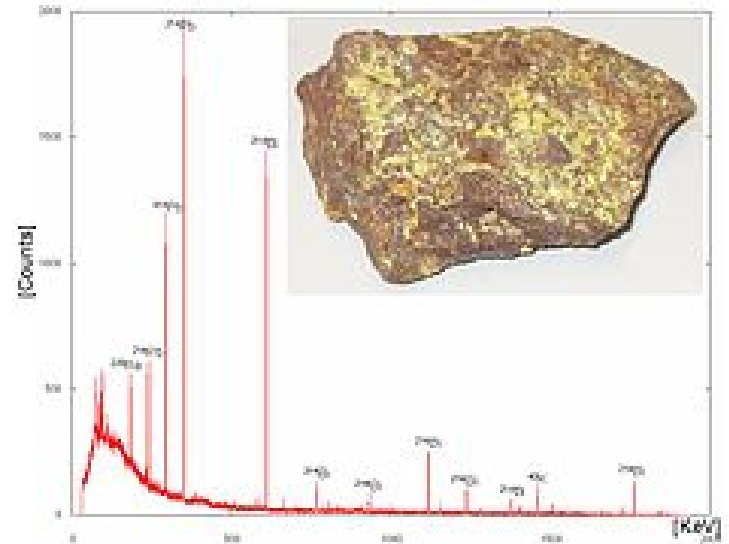


Use of Synchrotron Radiation in materials science

Gamma-rays



Decay scheme of ^{60}Co

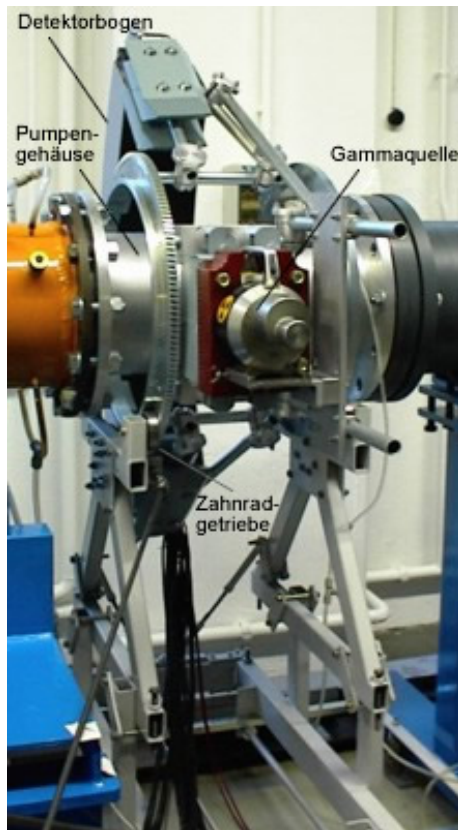


Gamma-ray spectrum of ^{238}U

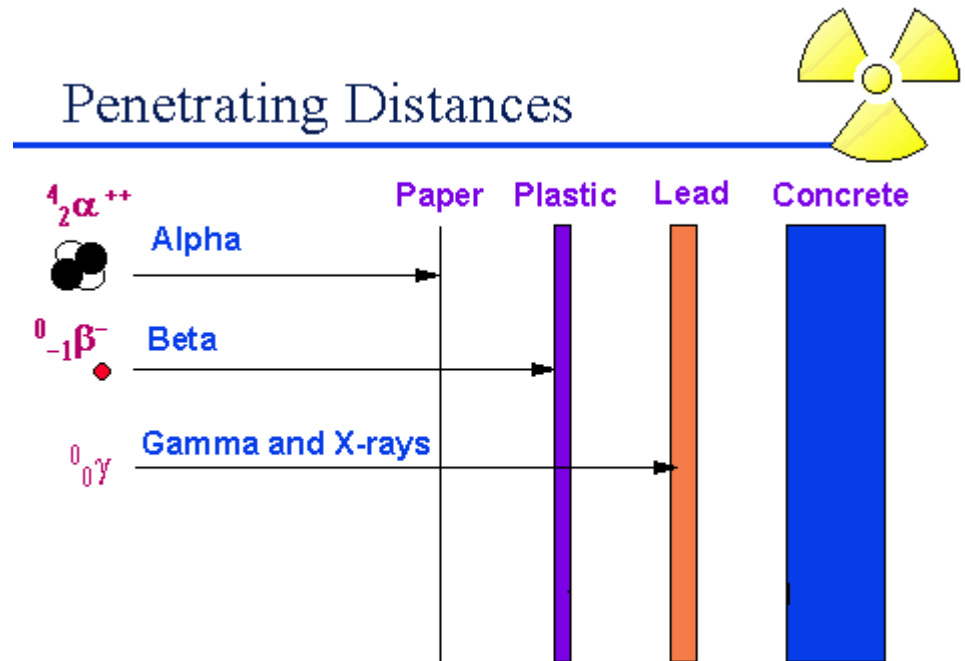
Gamma rays can occur whenever charged particles pass through magnetic fields or pass within certain distances of each other or by nuclear reactions (e.g. fusion or decay processes)

4.1 Electromagnetic radiation: Sources

Gamma-rays



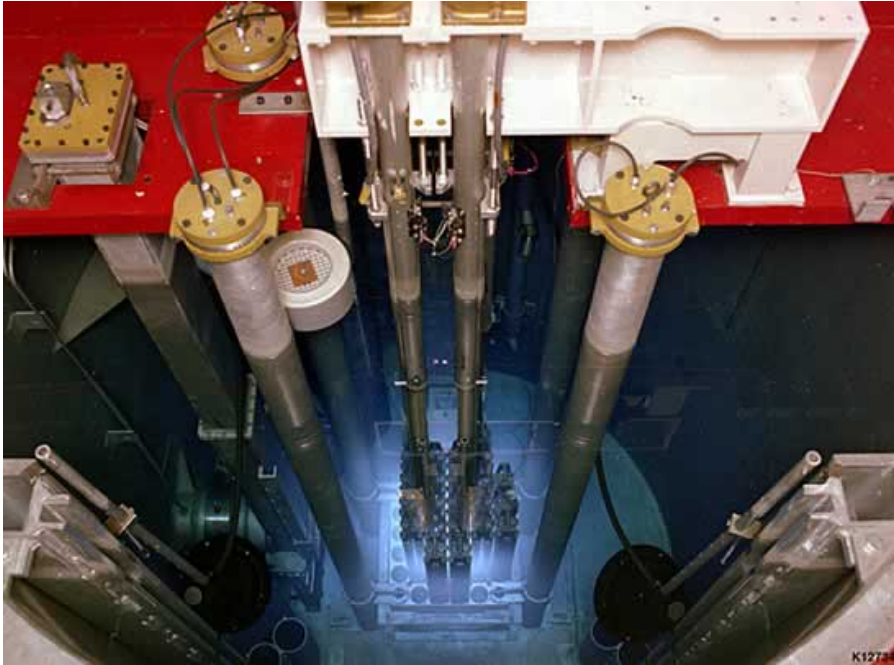
Gamma-radiation source



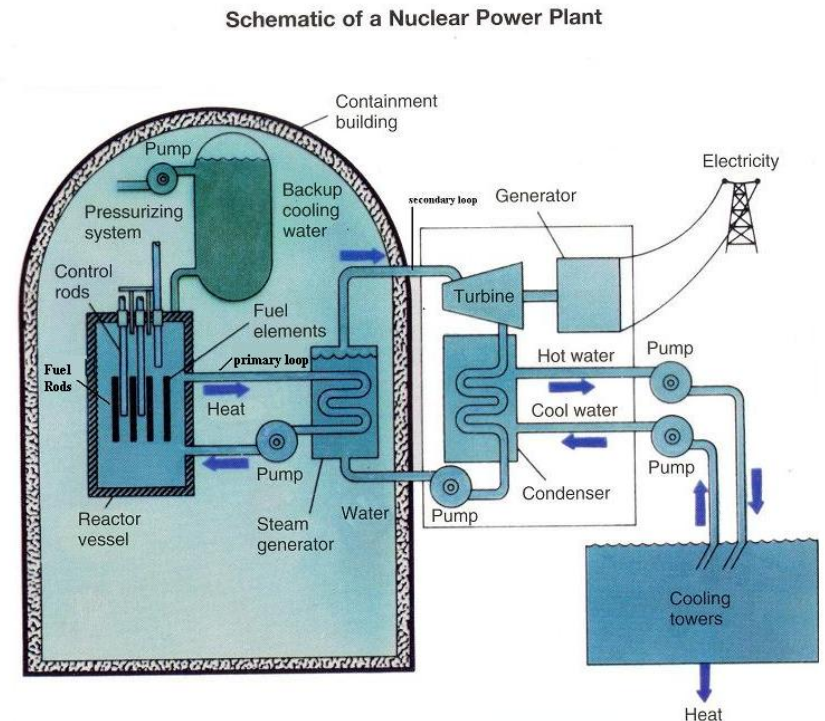
Nuclear decay products

4.1 Electromagnetic radiation: Sources

Neutrons



View into a nuclear reactor with Cherenkov radiation



Scetch of a nuclear power plant

De Broglie wave length: $\lambda = h/(m \cdot v)$
e.g. n with $v = 3.300 \text{ m/s} \rightarrow 0,05 \text{ eV} \rightarrow 1,2 \text{ \AA} \text{ (0,12 nm)}$

4.2 Microscopic techniques: OM, SEM, CTEM, HREM

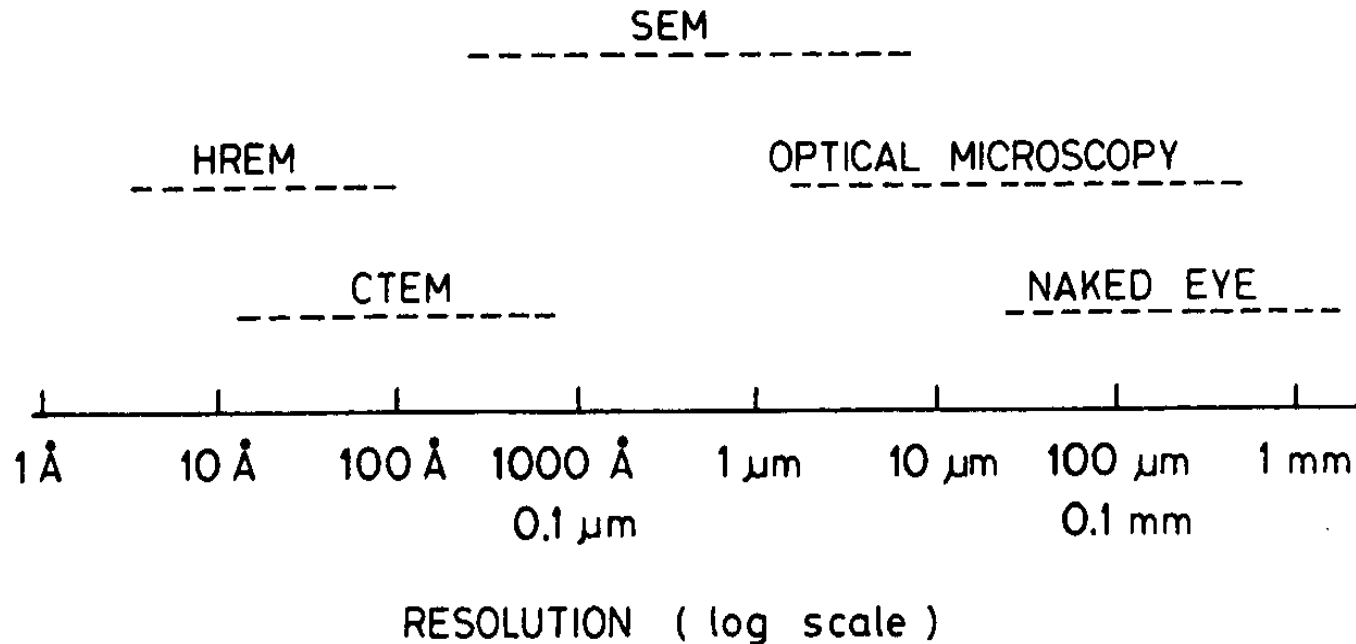


Fig. 4.2 Working ranges of various techniques used for viewing solids. CTEM = conventional transmission electron microscopy; HREM = high-resolution electron microscopy; SEM = scanning electron microscopy

4.3 Crystal structure analysis/determination

Analysis/determination of the crystal/molecular structure of a solid with the help of X-rays or neutrons means (because of the 3D periodicity of crystals):

Determination of

- the **geometry** (lattice constants $a, b, c, \alpha, \beta, \gamma$)
- the **symmetry** (space group)
- the **content** (typ, site x_j, y_j, z_j and thermal parameters B_j of the atoms j)

of the unit cell of a crystalline compound and their **analysis/interpretation** with respect to chemical or physical problems or questions.

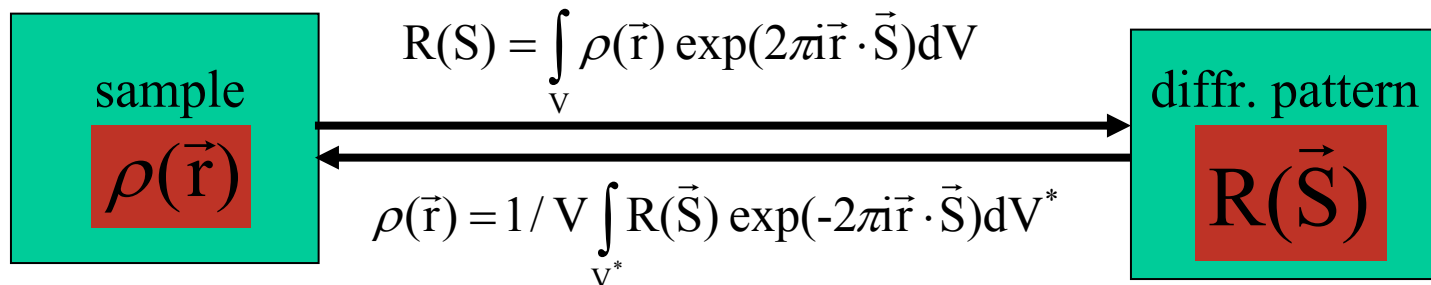
4.3 Crystal structure analysis/determination

is based on diffraction of electromagnetic radiation or neutrons of suitable energies/wavelengths/velocities and one needs:

- a crystalline sample (powder or single crystal, $V \sim 0.01 \text{ mm}^3$)
- an adequate electromagnetic radiation ($\lambda \sim 10^{-10} \text{ m}$)
- some knowledge of properties and diffraction of radiation
- some knowledge of structure and symmetry of crystals
- a diffractometer (with point and/or area detector)
- a powerful computer with the required programs for solution, refinement, analysis and visualization of the crystal structure
- some chemical feeling for interpretation of the results

4.3 Crystal structure analysis/determination

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

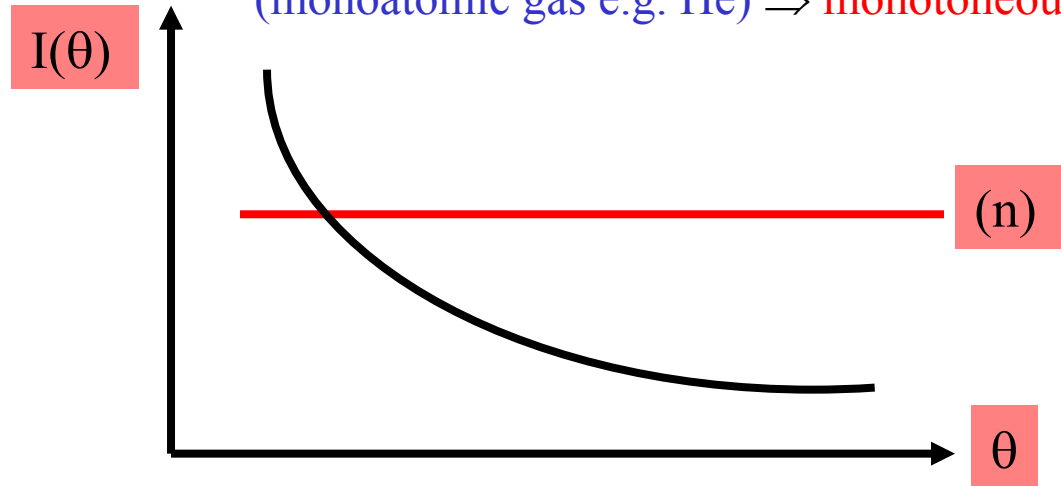


The shape of the resulting **scattering/diffraction pattern** depends on the **degree of order** of the sample.

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



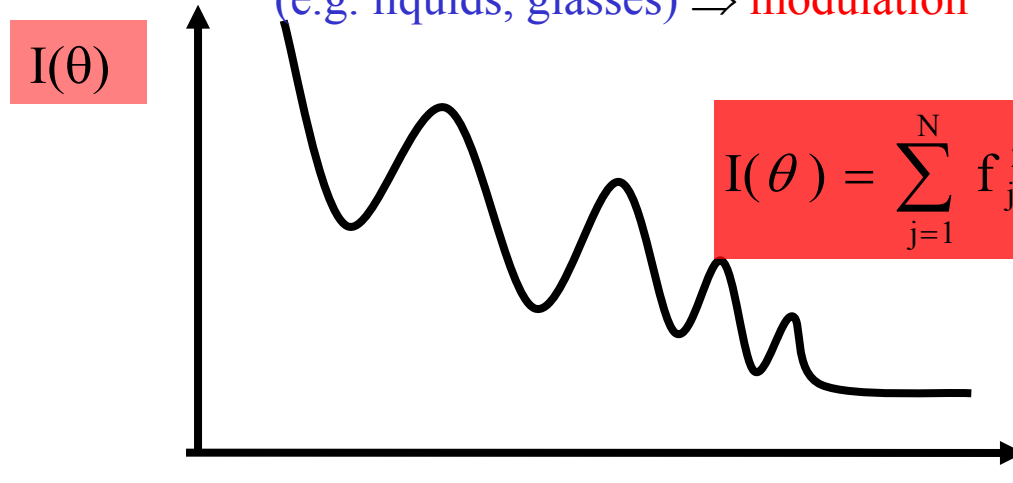
$$I(\theta) = N \cdot f^2$$

f = scattering length of atoms N

$\Rightarrow$ no information

no long-range, but short range order

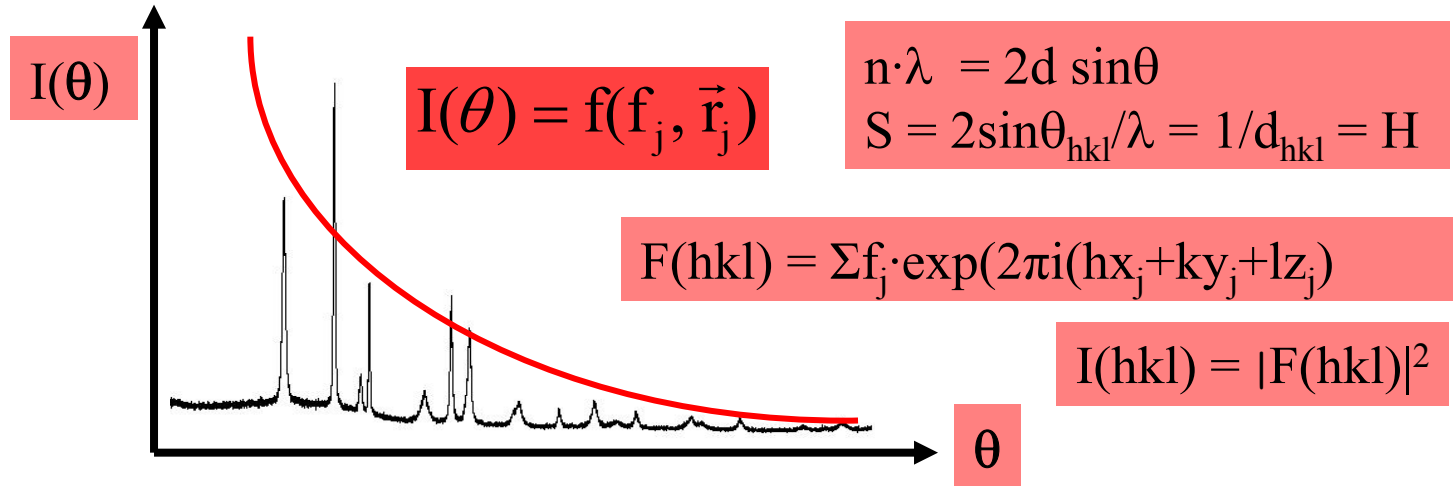
(e.g. liquids, glasses) $\Rightarrow$ modulation



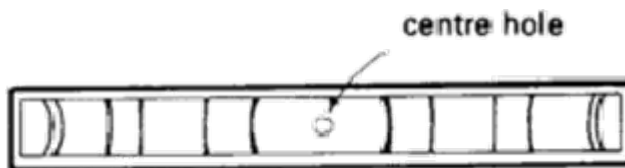
$$I(\theta) = \sum_{j=1}^N f_j^2 + 2 \sum_{j>} \sum_i f_j f_i \cos [\pi (\vec{r}_j - \vec{r}_i) \vec{S}]$$

$\Rightarrow$ radial distribution function
atomic distances

B. X-ray scattering diagram of a crystalline sample

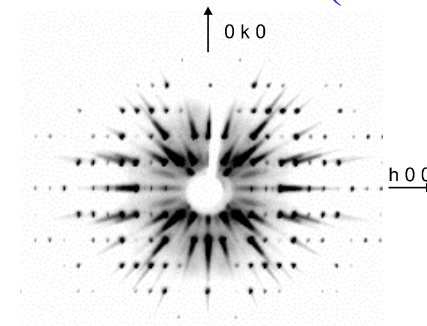


crystal powder
 orientation statistical, λ fixed
 $\Rightarrow$ cones of interference



Debye-Scherrer diagram

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

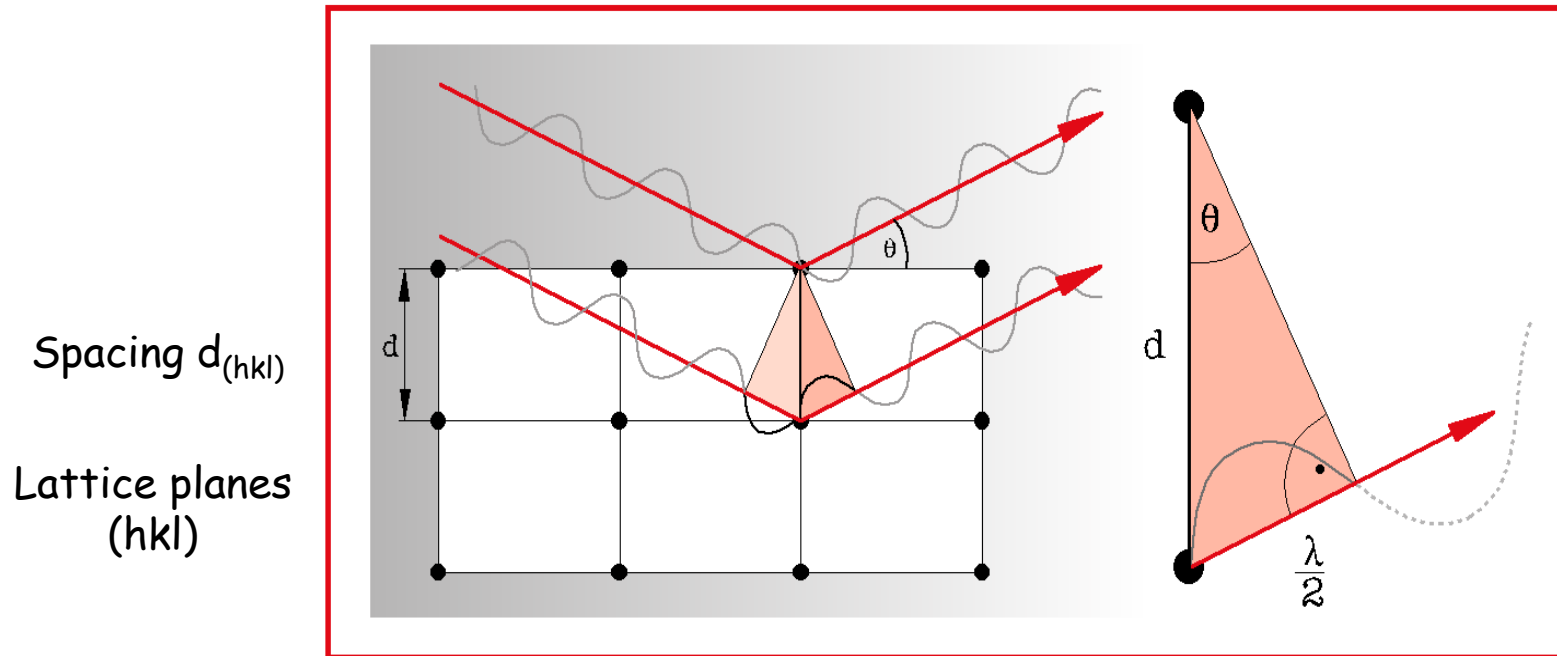


precession diagram

Why that?

4.3 Diffraction of X-rays or neutrons at a crystalline sample (single crystal or crystal powder)

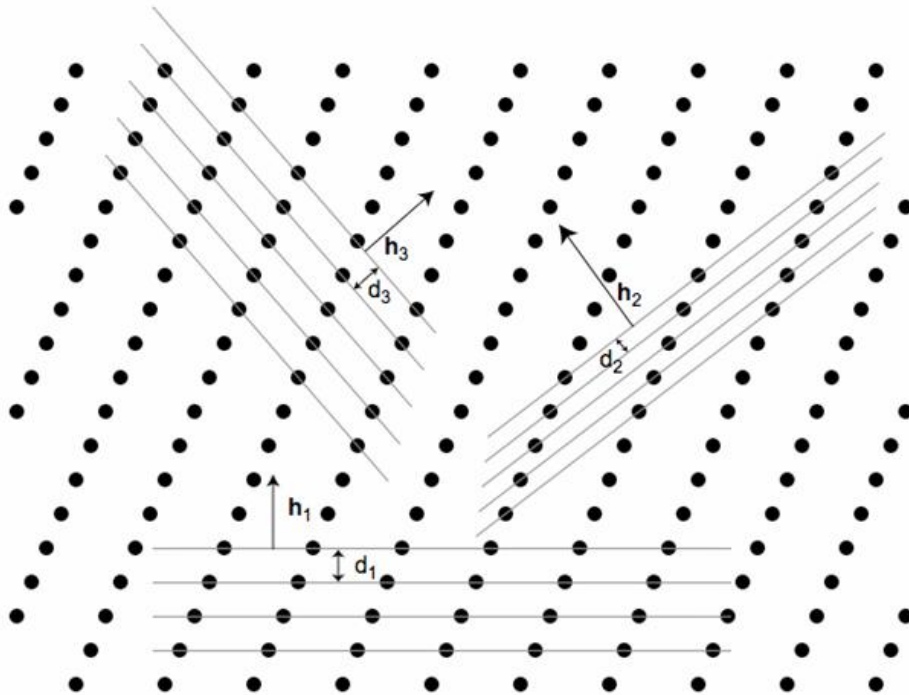
X-rays scattered from a crystalline sample are not totally extinct only for those directions, where the scattered rays are „in phase“.
 $R(S)$ und $I(\theta)$ therefore are periodic functions of „Bragg reflections“ .



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

4.3 Basic equation of X-ray analysis: Bragg equation

Lattice planes: Why are they important ?

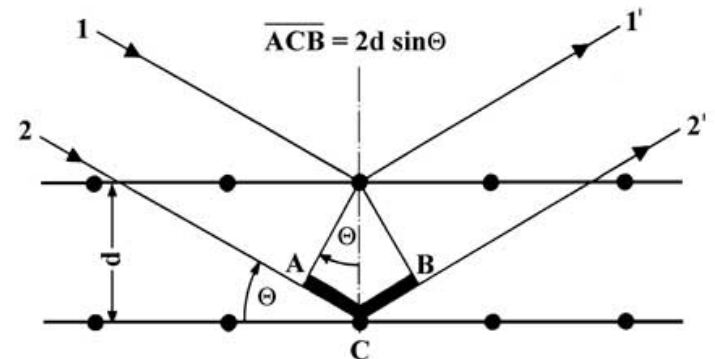
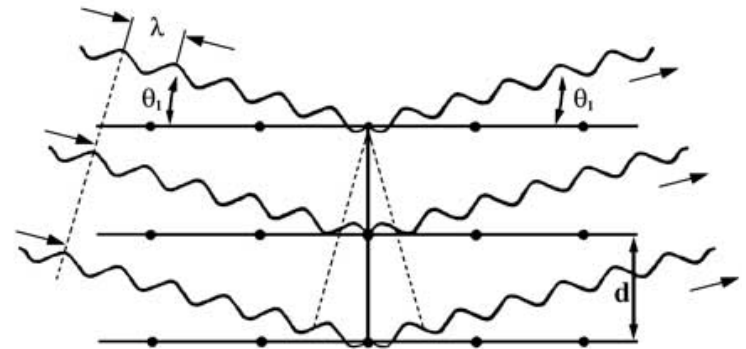


Question: How are directions and planes in a regular lattice defined ?

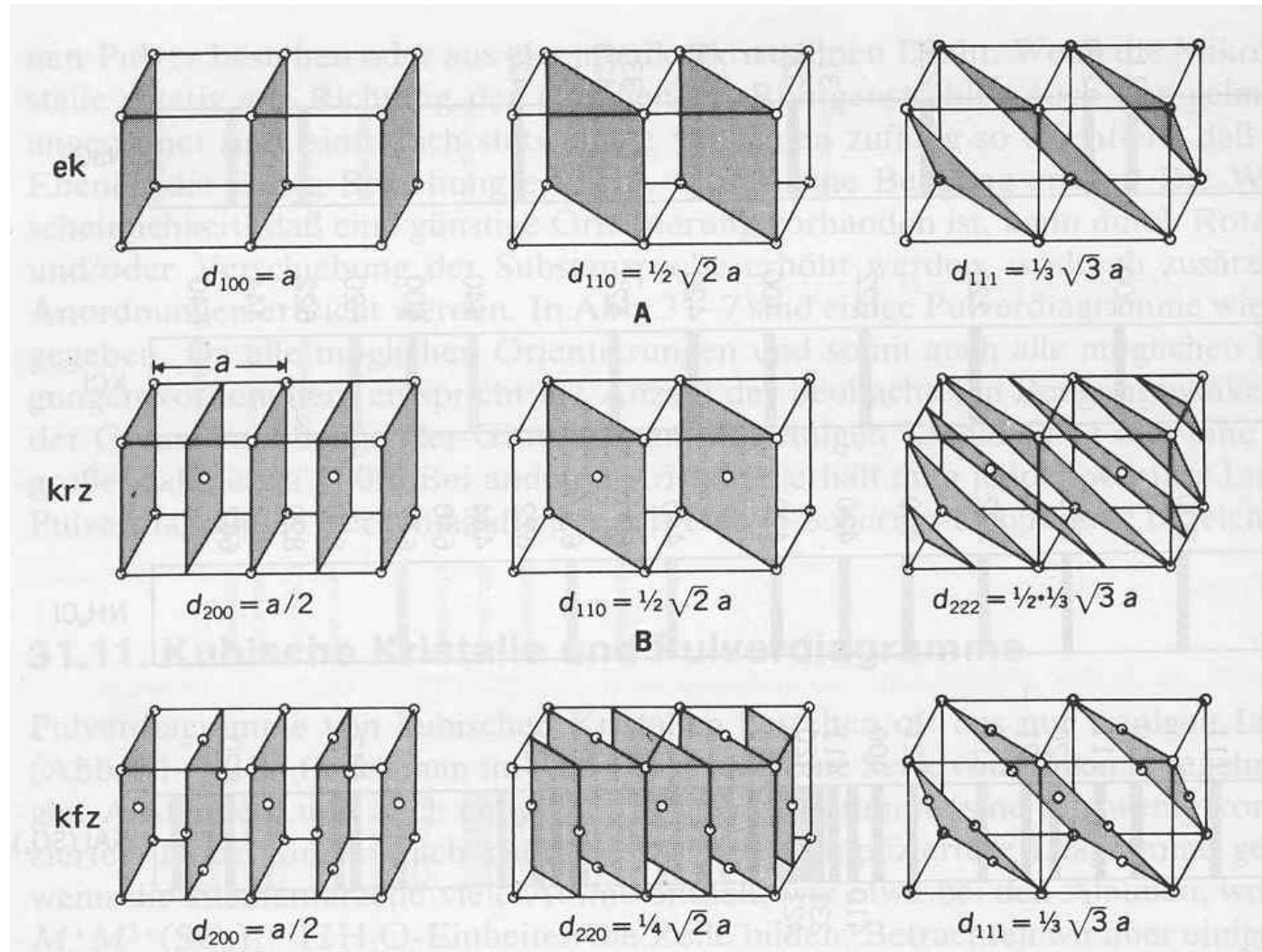
Bragg equation:

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

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

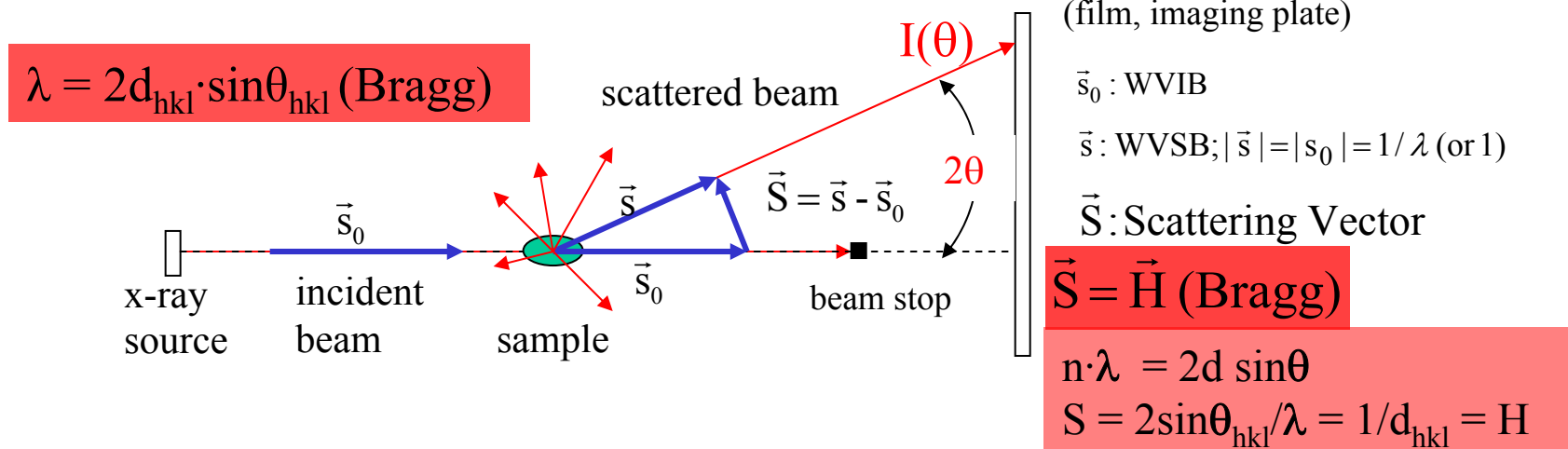


Lattice plane series: Miller indices hkl, d values

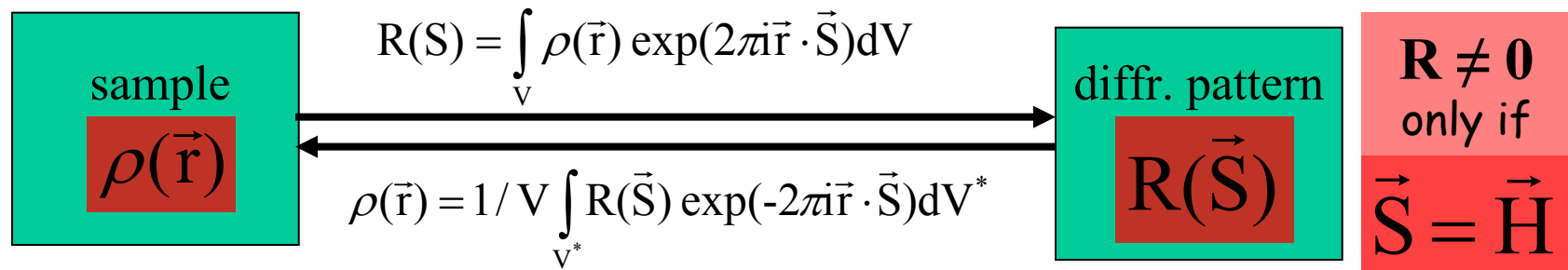


(X-ray) diffraction of a crystalline sample

(single crystal or crystal powder)



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

4.3 Crystal structure analysis/determination

Analysis/determination of the crystal/molecular structure of a **crystalline solid** with the help of X-rays or neutrons therefore means:

Determination of

- the **geometry** (lattice constants $a, b, c, \alpha, \beta, \gamma$)
- the **symmetry** (space group)
- the **content** (type, site x_j, y_j, z_j and thermal parameters B_j of the atoms j)

of the unit cell of that crystalline compound from the scattering/diffraction pattern **$R(S)$ or $I(\theta)$ or $I(hkl)$**

How does that work?

4.3 Crystal structure analysis/determination

- The **geometry** (lattice constants $a, b, c, \alpha, \beta, \gamma$) of the unit cell/ compound one can get from the **geometry of the diffraction pattern**, i.e. from the **site of the reflections** (diffraction angles θ for a powder; „Euler angles“ $\theta, \omega, \varphi, \chi$ for a single crystal)
- The **symmetry** (space group) one can get from the **symmetry of the reflections** and the **systematically extinct reflections**,
- The **content** of the unit cell (typ, site x_j, y_j, z_j and thermal parameters B_j of the atoms j) one can get from the **intensities $I(hkl)$ of the reflections** and the respective **phases $\alpha(hkl)$** .

$$|F_o(hkl)| \approx (I(hkl))^{1/2} \quad F_c(hkl) = \sum f_j \cdot \exp(2\pi i(hx_j + ky_j + lz_j))$$
$$\delta(xyz) = (1/V) \cdot \sum |F_o(hkl)| \cdot \exp(i\alpha(hkl)) \cdot \exp(-2\pi i(hx + ky + lz))$$

The structure factor is named **$F_o(hkl)$** , if observed, i.e. derived from measured $I(hkl)$ and **$F_c(hkl)$** if calculated from f_j, x_j, y_j, z_j . Note that **(hkl)** represent lattice planes and **hkl** reflections.

4.3 Crystal structure analysis/determination

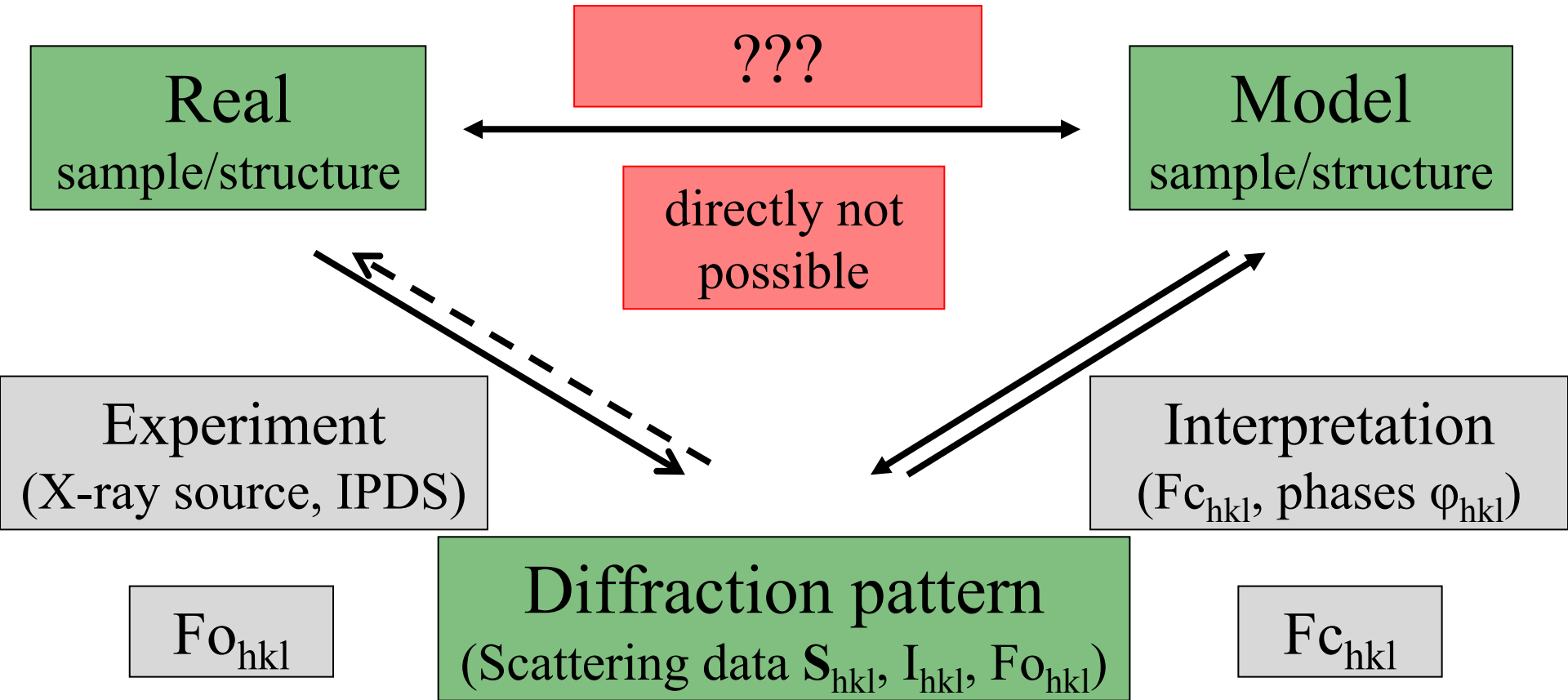
- The **intensity** I_{hkl} of the reflections (i.e. of the reciprocal lattice points) thus reflect the atomic arrangement of the **real crystal structure**.
- Each **intensity** $I(hkl)$ or I_{hkl} is proportional to the **square** of a quantity called **structure factor** $F(hkl)$ or F_{hkl} (F_o for observed, F_c for calculated).
- The structure factor $F(hkl)$ is a **complex number** in general but becomes **real** in case of crystal structures with a **centre of symmetry**:

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

- In case of centrosymmetric crystal structures, the phases are 0 or π , i.e. „only“ the signs instead of the phases of the structure factors have to be determined.

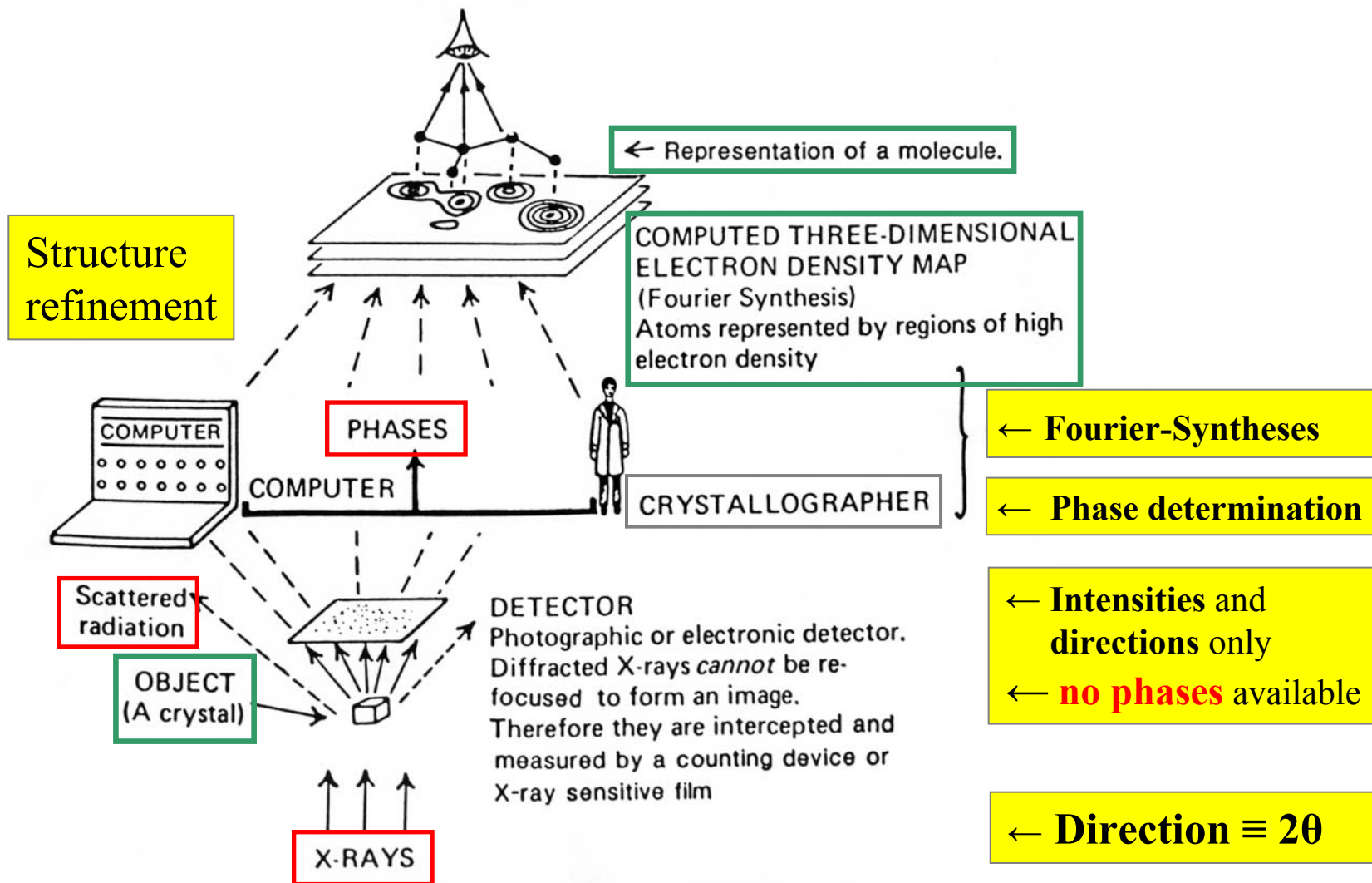
The problem is that the **phases/signs** are lost upon measurement of the intensities of the reflections (**phase problem** of crystal structure analysis/determination)

4.3 Crystal structure analysis/determination



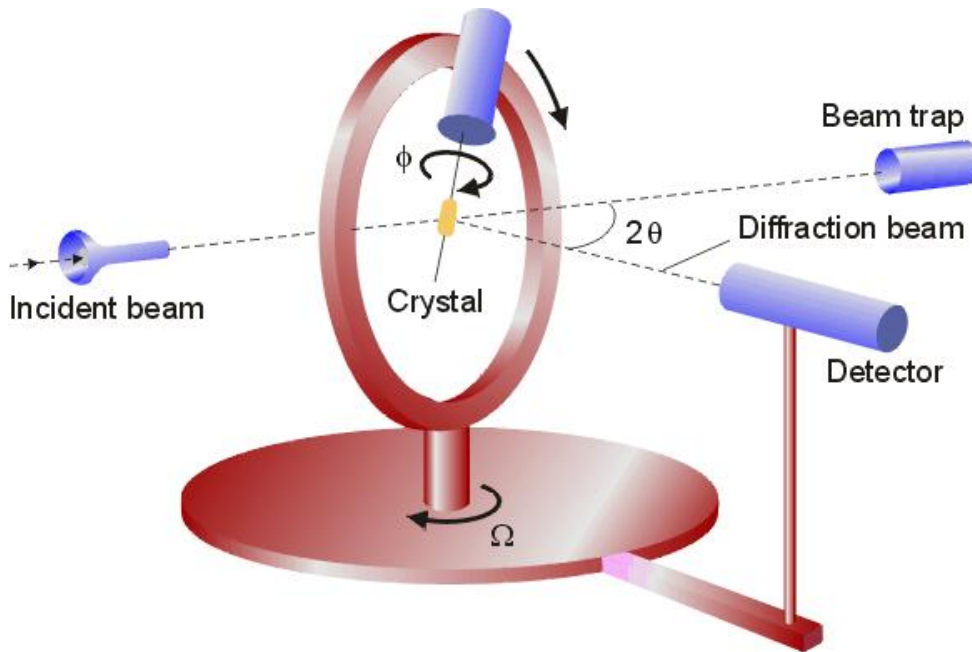
Structure determination only indirectly possible!

4.3 Crystal structure analysis/determination



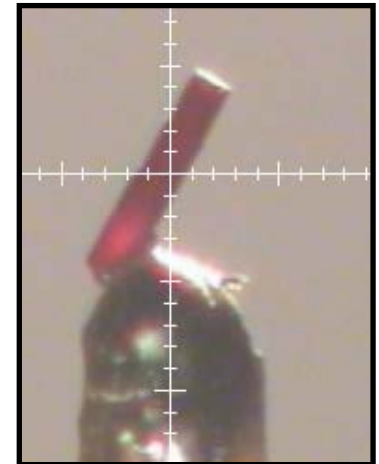
Realisation of a crystal structure determination

1. Fixing und centering of a crystal on a diffractometer and determination of the **orientaion matrix** M and the **lattice constants** $a, b, c, \alpha, \beta, \gamma$ of the crystal from the Eulerian angles of the reflections $(\theta, \omega, \phi, \chi)$ and of the **cell content number** Z (aus cell volume, density and formula),

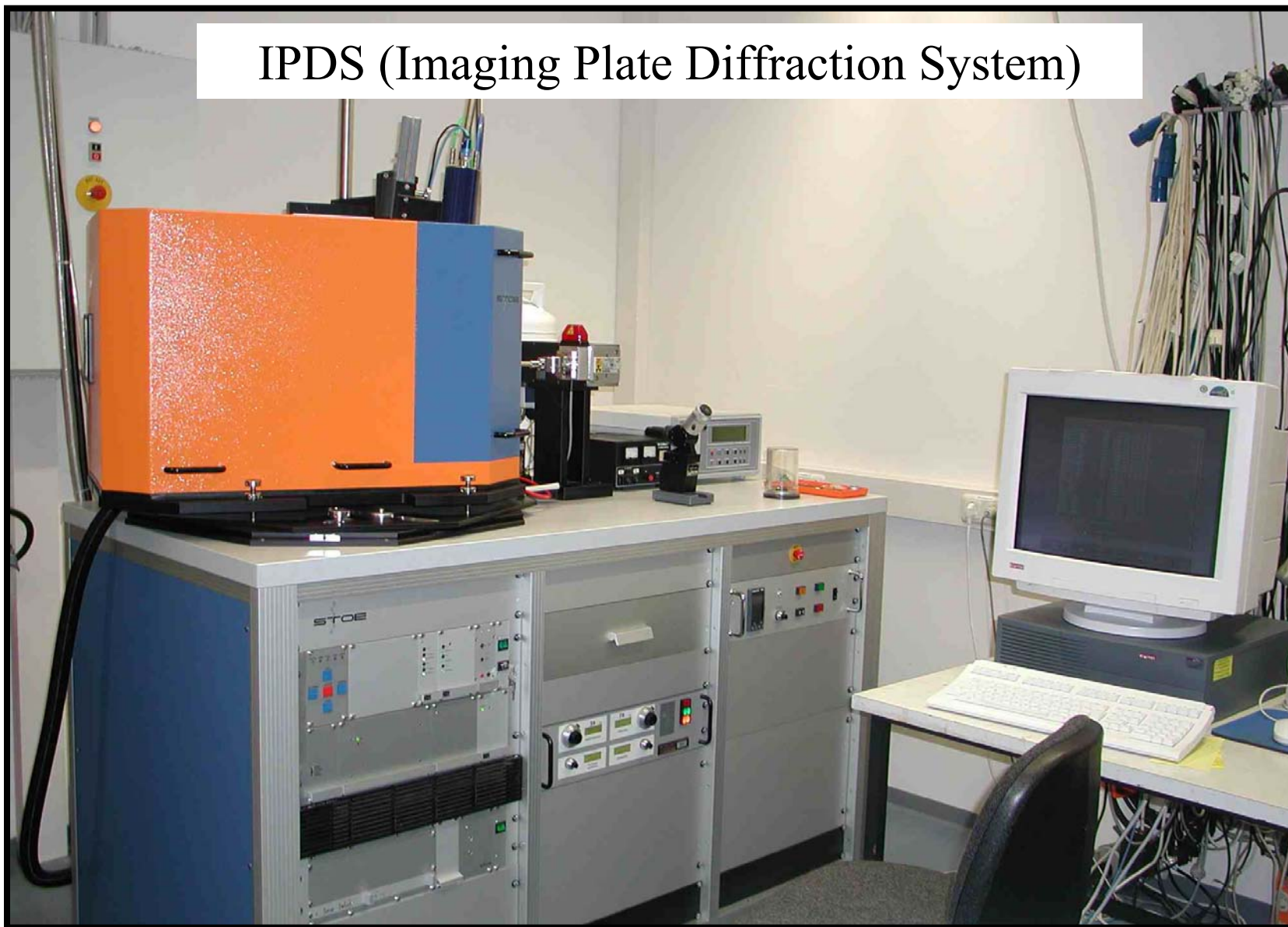


Principle of a four-circle diffraktometer for single crystal stucture determination by use of X-ray or neutron diffraction

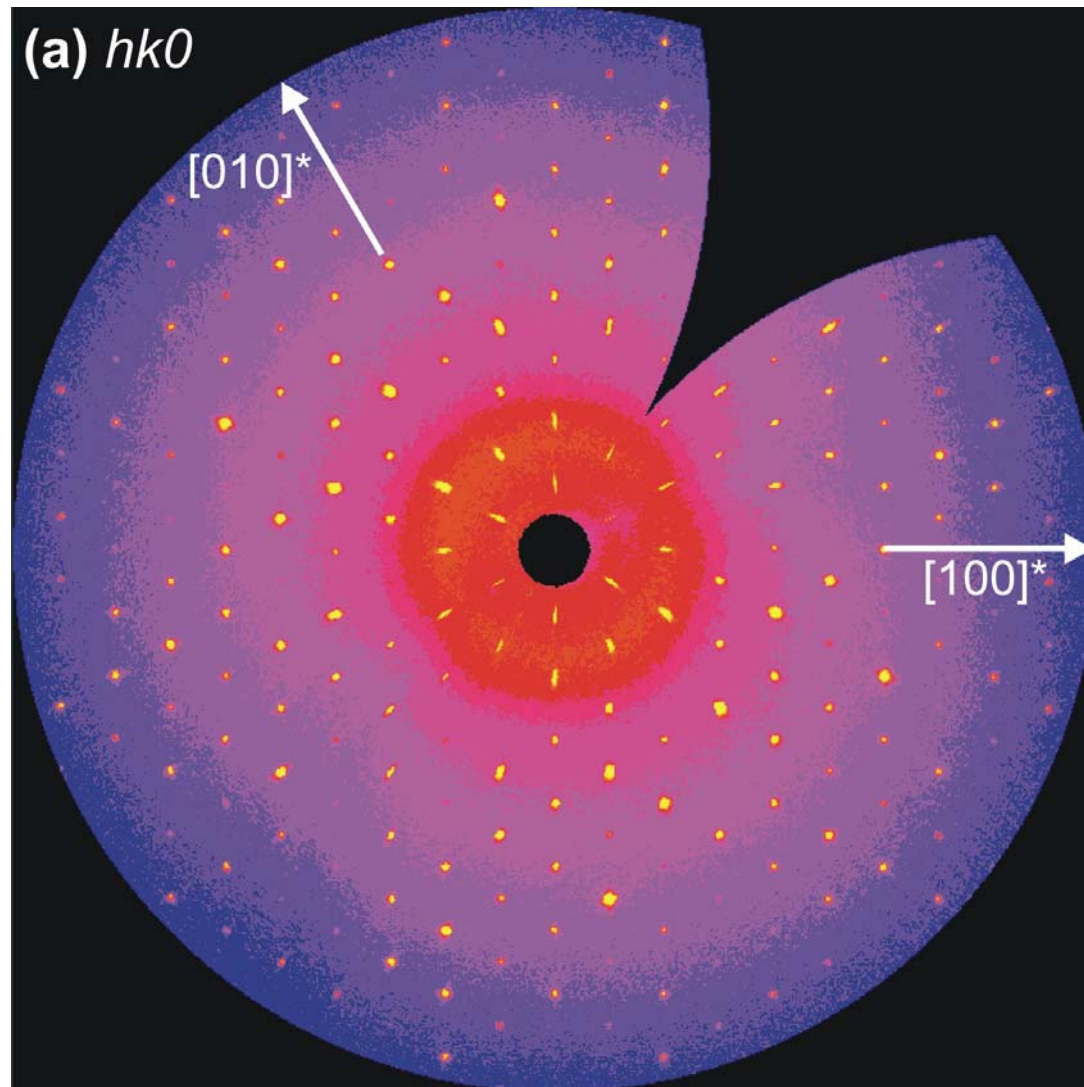
CAD4 (Kappa-Axis-Diffraktometer)



IPDS (Imaging Plate Diffraction System)



4.3 X-ray analysis with single crystals: Reciprocal lattice (calculated from an IPDS measurement)



Realisation of a crystal structure determination

2. Determination of the space group (from symmetry and systematic extinctions of the reflections)
3. Measuring of the **intensities** $I(hkl)$ of the reflections (asymmetric part of the reciprocal lattice up to $0.5 \leq \sin\theta/\lambda \leq 1.1$ is sufficient)
4. Calculation of the **structure amplitudes** $|F_{o_{hkl}}|$ from the I_{hkl} incl. absorption, extinction, LP correction $\rightarrow$ **data reduction**
5. Determination of the **scale factor** K and of the mean **temperature parameter** B for the compound under investigation from the mean $|F_{o_{hkl}}|$ values for different small θ ranges θ_m according to $\ln(|F_o|^2/\Sigma f_j^2) = \ln(1/K) - 2B(\sin^2\theta_m)/\lambda^2 \rightarrow$ **data scaling**

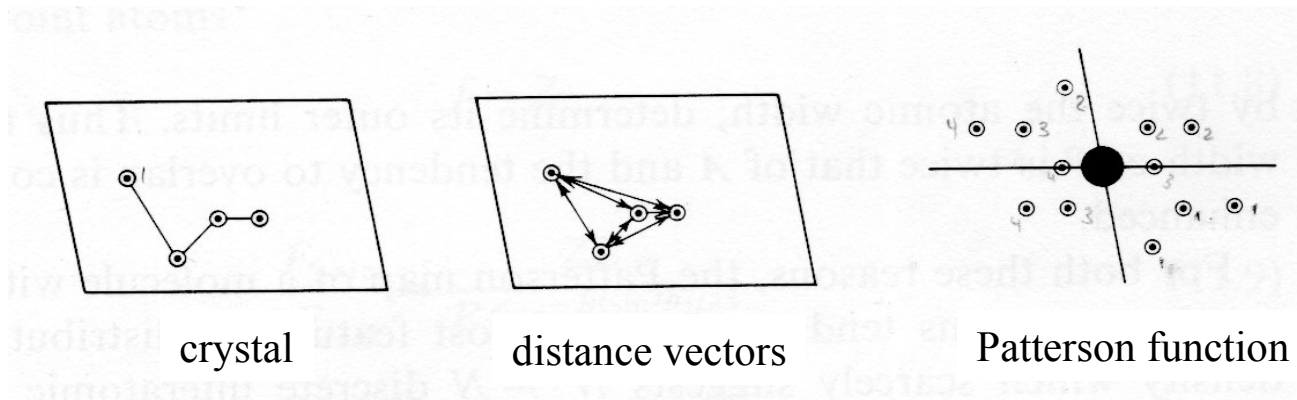
Realisation of a crystal structure determination

6a. Determin. of the **phases** α_{hkl} of the **structure amplitudes** $|F_{o_{hkl}}|$
→ **phase determination** (**phase problem of structure analysis**)

- trial and error (model, than proof of the scattering pattern)
- calculation of the **Patterson function**

$$P_{(uvw)} = (1/V) \cdot \sum |F_{hkl}|^2 \cos 2\pi(hu + kv + lw)$$

from the **structure amplitudes** resulting in **distance vectors**
between all atoms of the unit cell



Points to the distribution and position of „heavy atoms“
in the unit cell → **heavy atom method**

Realisation of a crystal structure determination

6b. Determin. of the **phases** α_{hkl} of the **structure amplitudes** $|F_{o_{hkl}}|$

- **direct methodes** for phase determination

phases α_{hkl} and intensity distribution are not independent from each other $\rightarrow$ allows determination of the phases α_{hkl}

e.g. $F(hkl) \sim \sum \sum \sum F(h'k'l') \cdot F(h-h', k-k', l-l')$ (Sayre, 1952)

oder $S(F_{hkl}) \sim S(F_{h'k'l'}) \cdot S(F_{h-h', k-k', l-l'})$ ($S = \text{sign of } F$)

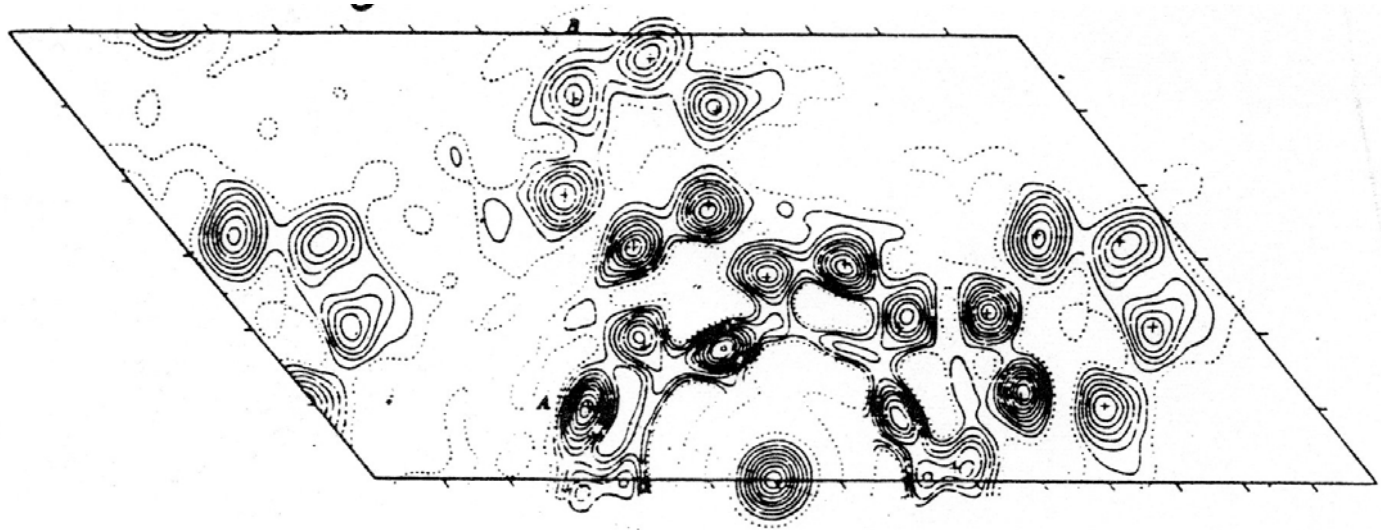
direct methodes today are the most important methodes for the solving the phase problem of structure analysis/determination

- anomalous dispersion methodes use the phase and intensity differences in the scattering near and far from absorption edges (measuring with X-rays of different wave lengths necessary)

Realisation of a crystal structure determination

7. Calculation of the **electron density distribution function**

$\delta(xyz) = (1/V) \cdot \sum |F_{o_{hkl}}| \cdot \exp(i\alpha_{hkl}) \cdot \exp(-2\pi i(hx+ky+lz))$ of the unit cell from the **structure amplitudes** $|F_{o_{hkl}}|$ and the **phases** α_{hkl} of the reflections hkl (using B and K) $\rightarrow$ **Fourier synthesis**



Platin-Phthalocyanin, $\text{PtC}_{32}\text{H}_{16}\text{N}_8$: Elektronendichteprojektion $\rho(xz)$.

and determination of the elements and the atom sites x_j, y_j, z_j

Realisation of a crystal structure determination

8. Calculation of the **structure factors** $F_{c_{hkl}}$ (c: calculated) by use of these atomic sites/coordinates x_j, y_j, z_j and the **atomic form factors** (atomic scattering factors) f_j according to

$$F_{c_{hkl}} = \sum f_j \cdot \exp(2\pi i(hx_j + ky_j + lz_j))$$

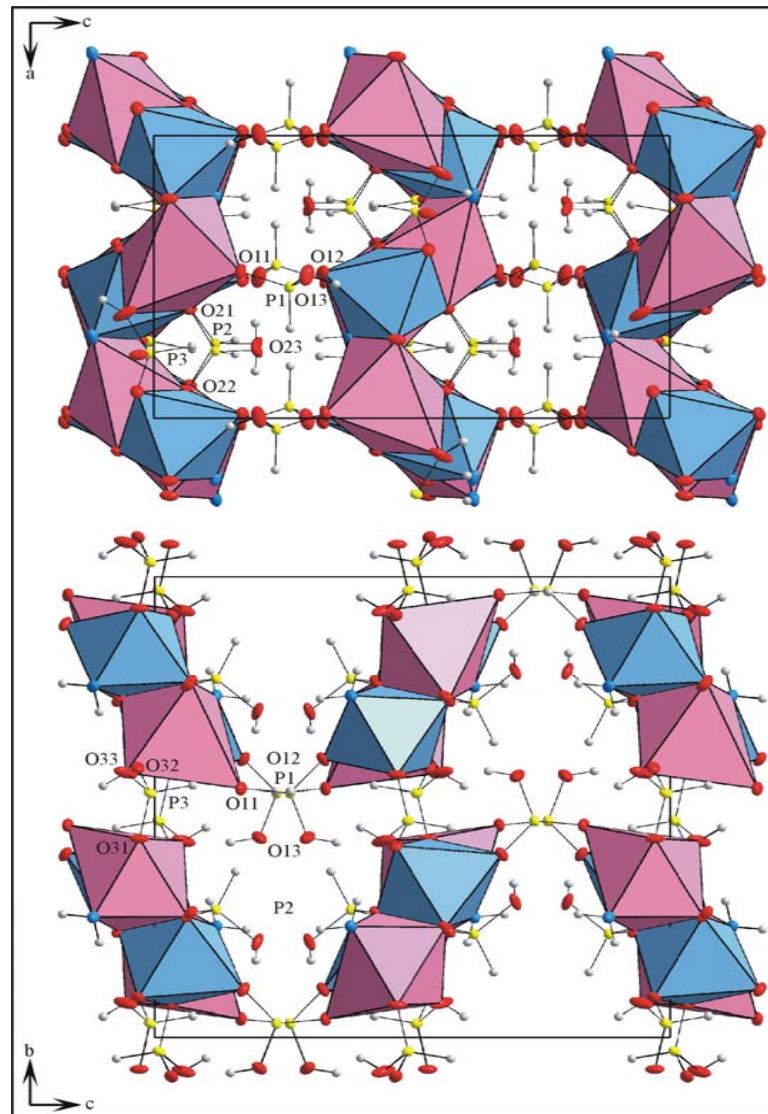
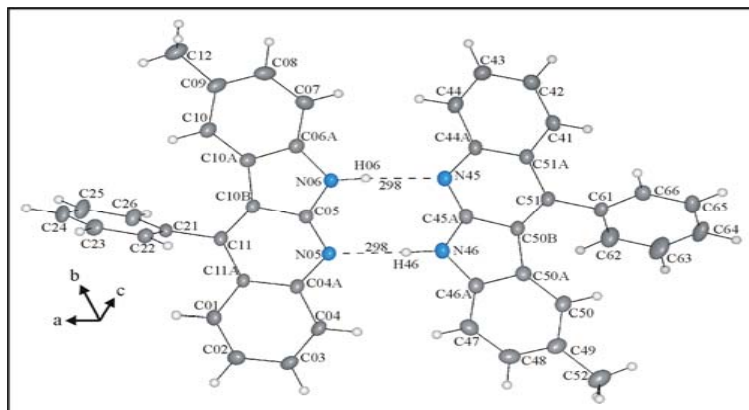
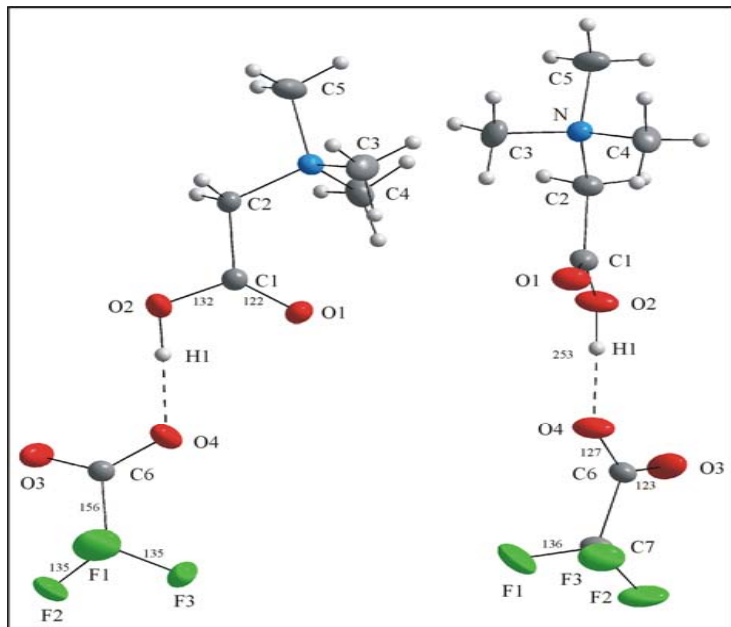
9. **Refinement** of the **scale factor** K , the **temperature parameter** B (or of the individual B_j of the atoms j of the unit cell) and of the **atomic coordinates** x_j, y_j, z_j by use of the least squares method, LSQ via minimising the function

$$(\Delta F)^2 = (|F_o| - |F_c|)^2 \text{ for all measured reflections } hkl$$

agreement factor: $R = \sum (|F_o| - |F_c|) / \sum |F_o|$

10. Calculation of the **bond lengths and angles** etc. and graphical visualisation of the structure (structure plot)

Results



Results

Crystallographic and structure refinement data of $\text{Cs}_2\text{Co}(\text{HSeO}_3)_4 \cdot 2\text{H}_2\text{O}$

Name	Figure		Name	Figure
Formula	$\text{Cs}_2\text{Co}(\text{HSeO}_3)_4 \cdot 2\text{H}_2\text{O}$		Diffractometer	IPDS (Stoe)
Temperature	293(2) K		Range for data collection	$3.1^\circ \leq \Theta \leq 30.4^\circ$
Formula weight	872.60 g/mol		<i>hkl</i> ranges	$-10 \leq h \leq 10$
Crystal system	Monoclinic			$-17 \leq k \leq 18$
Space group	$P 2_1/c$			$-10 \leq l \leq 9$
Unit cell dimensions	$a = 757.70(20)$ pm		Absorption coefficient	$\mu = 15.067 \text{ mm}^{-1}$
	$b = 1438.80(30)$ pm		No. of measured reflections	9177
	$c = 729.40(10)$ pm		No. of unique reflections	2190
	$\beta = 100.660(30)^\circ$		No. of reflections ($I_0 \geq 2\sigma(I)$)	1925
Volume	$781.45(45) \times 10^6 \text{ pm}^3$		Extinction coefficient	$\varepsilon = 0.0064$
Formula units per unit cell	$Z = 2$		$\Delta\rho_{\min} / \Delta\rho_{\max} / \text{e/pm}^3 \times 10^{-6}$	-2.128 / 1.424
Density (calculated)	3.71 g/cm^3		R_1 / wR_2 ($I_0 \geq 2\sigma(I)$)	0.034 / 0.081
Structure solution	SHELXS – 97		R_1 / wR_2 (all data)	0.039 / 0.083
Structure refinement	SHELXL – 97		Goodness-of-fit on F^2	1.045
Refinement method	Full matrix LSQ on F^2			

Results

Positional and isotropic atomic displacement parameters of $\text{Cs}_2\text{Co}(\text{HSeO}_3)_4 \cdot 2\text{H}_2\text{O}$

Atom	WP	x	y	z	$U_{\text{eq}}/\text{pm}^2$
Cs	4e	0.50028(3)	0.84864(2)	0.09093(4)	0.02950(11)
Co	2a	0.0000	1.0000	0.0000	0.01615(16)
Se1	4e	0.74422(5)	0.57877(3)	0.12509(5)	0.01947(12)
O11	4e	0.7585(4)	0.5043(3)	0.3029(4)	0.0278(7)
O12	4e	0.6986(4)	0.5119(3)	-0.0656(4)	0.0291(7)
O13	4e	0.5291(4)	0.6280(3)	0.1211(5)	0.0346(8)
H11	4e	0.460(9)	0.583(5)	0.085(9)	0.041
Se2	4e	0.04243(5)	0.67039(3)	-0.18486(5)	0.01892(12)
O21	4e	-0.0624(4)	0.6300(2)	-0.3942(4)	0.0229(6)
O22	4e	0.1834(4)	0.7494(3)	-0.2357(5)	0.0317(7)
O23	4e	-0.1440(4)	0.7389(2)	-0.1484(4)	0.0247(6)
H21	4e	-0.120(8)	0.772(5)	-0.062(9)	0.038
OW	4e	-0.1395(5)	1.0685(3)	0.1848(5)	0.0270(7)
HW1	4e	-0.147(8)	1.131(5)	0.032	0.032
HW2	4e	-0.159(9)	1.045(5)	0.247(9)	0.032

Results

Anisotropic thermal displacement parameters $U_{ij} \times 10^4 / \text{pm}^2$ of $\text{Cs}_2\text{Co}(\text{HSeO}_3)_4 \cdot 2\text{H}_2\text{O}$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cs	0.0205(2)	0.0371(2)	0.0304(2)	0.00328(9)	0.0033(1)	-0.00052(1)
Co	0.0149(3)	0.0211(4)	0.0130(3)	0.0006(2)	0.0041(2)	0.0006(2)
Se1	0.0159(2)	0.0251(3)	0.01751(2)	-0.00089(1)	0.00345(1)	0.00097(1)
O11	0.0207(1)	0.043(2)	0.0181(1)	-0.0068(1)	-0.0013(1)	0.0085(1)
O12	0.0264(2)	0.043(2)	0.0198(1)	-0.0009(1)	0.0089(1)	-0.0094(1)
O13	0.0219(1)	0.034(2)	0.048(2)	0.0053(1)	0.0080(1)	-0.009(2)
Se2	0.0179(2)	0.0232(2)	0.0160(2)	0.00109(1)	0.00393(1)	-0.0001(1)
O21	0.0283(1)	0.024(2)	0.0161(1)	0.0008(1)	0.0036(1)	-0.0042(1)
O22	0.0225(1)	0.032(2)	0.044(2)	-0.0058(1)	0.0147(1)	-0.0055(1)
O23	0.0206(1)	0.030(2)	0.0240(1)	0.0018(1)	0.0055(1)	-0.0076(1)
OW	0.0336(2)	0.028(2)	0.0260(2)	0.0009(1)	0.0210(1)	-0.0006(1)

The anisotropic displacement factor is defined as: $\exp \{-2\pi^2[U_{11}(ha^*)^2 + \dots + 2U_{12}hka^*b^*]\}$

Results

Some selected bond lengths (/pm) and angles(/°) of $\text{Cs}_2\text{Co}(\text{HSeO}_3)_4 \cdot 2\text{H}_2\text{O}$

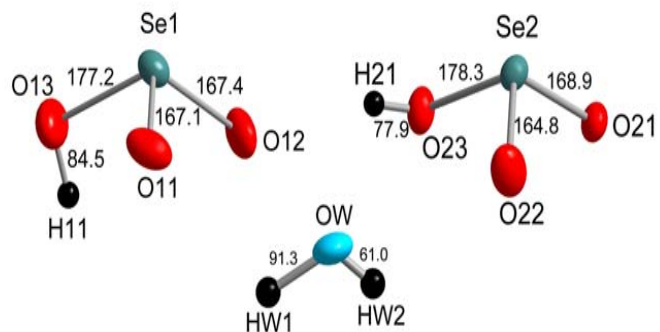
CsO₉ polyhedron			
Cs-O11	316.6(3)	O22-Cs-OW	78.76(8)
Cs-O13	318.7(4)	O22-Cs-O12	103.40(9)
Cs-O22	323.7(3)	O23-Cs-O11	94.80(7)
Cs-O23	325.1(3)	O13-Cs-O11	42.81(8)
Cs-OW	330.2(4)	O11-Cs-O23	127.96(8)
Cs-O21	331.0(3)	O13-Cs-O22	65.50(9)
Cs-O12	334.2(4)	O22-Cs-O22	66.96(5)
Cs-O22	337.1(4)	O11-Cs-OW	54.05(8)
Cs-O13	349.0(4)	O23-Cs-O22	130.85(9)
CoO₆ octahedron			
Co-OW	210.5(3)	OW-Co-OW	180
Co-O11	210.8(3)	OW-Co-O21	90.45(13)
Co-O21	211.0(3)	OW-Co-O11	89.55(13)

SeO₃²⁻ anions				
Se1-O11	167.1(3)	O12- Se1-O11	104.49(18)	
Se1-O12	167.4(3)	O12- Se1-O13	101.34(18)	
Se1-O13	177.2(3)	O11- Se1-O13	99.66(17)	
Se2-O21	168.9(3)	O22- Se2-O21	104.46(17)	
Se2-O22	164.8(3)	O22- Se2-O23	102.51(17)	
Se2-O23	178.3(3)	O21- Se2-O23	94.14(15)	
Hydrogen bonds		d(O-H)	d(O...H)	d(O...O)
O13-H11...O12	85(7)	180(7)	263.3(5)	166(6)
O23-H21...O21	78(6)	187(7)	263.7 (4)	168(7)
OW-HW1...O22	91(7)	177(7)	267.7 (5)	174(6)
OW-HW2...O12	61(6)	206(6)	264.3 (4)	161(8)

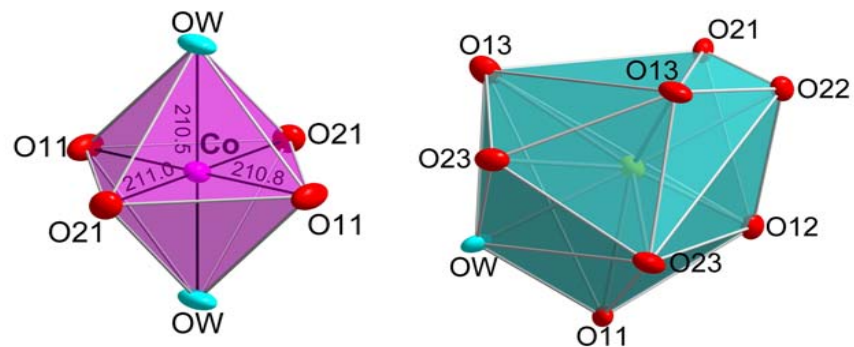
Symmetry codes:

- | | | |
|-----------------------|------------------------|------------------------|
| 1. -x, -y+2, -z | 2. -x+1, -y+2, -z | 3. -x+1, y-1/2, -z+1/2 |
| 4. x-1, -y+3/2, z-1/2 | 5. x, -y+3/2, z-1/2 | 6. x, -y+3/2, z+1/2 |
| 7. -x, y-1/2, -z-1/2 | 8. -x+1, y+1/2, -z+1/2 | 9. x+1, -y+3/2, z+1/2 |
| 10. -x, y+1/2, -z-1/2 | 11. -x+1, -y+1, -z | 12. x-1, -y+3/2, z+1/2 |

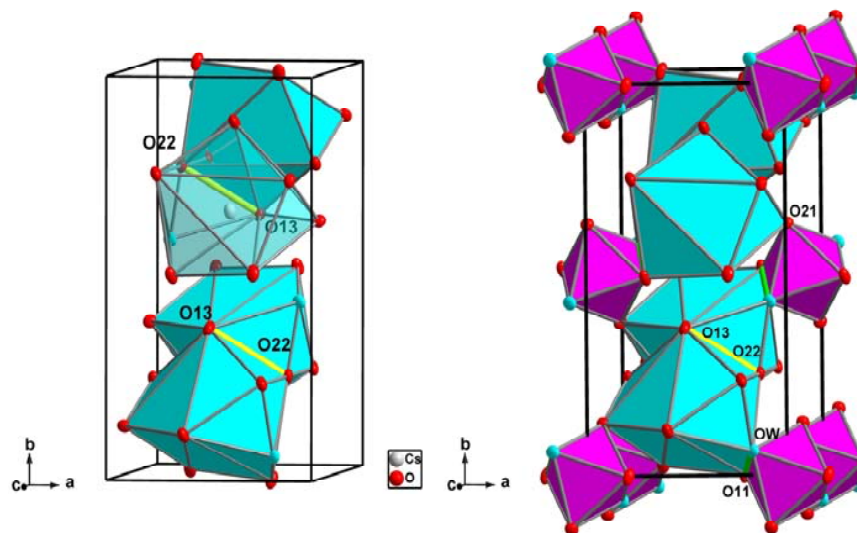
Results



Molecular units of $\text{Cs}_2\text{Co}(\text{HSeO}_3)_4 \cdot 2\text{H}_2\text{O}$

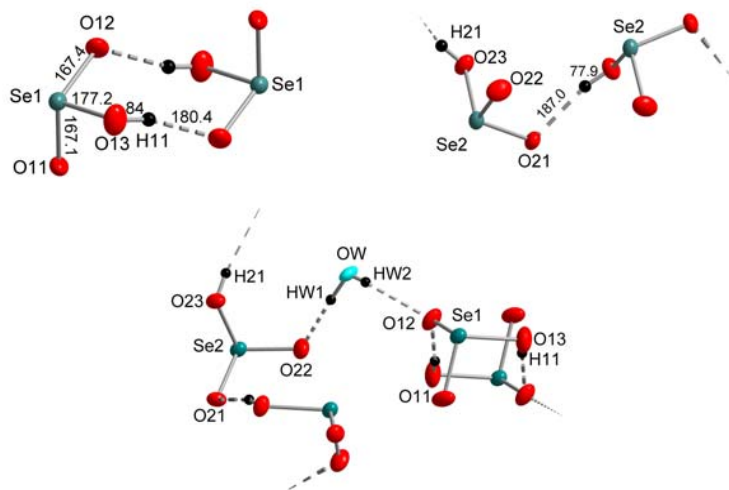


Coordination polyhedra of $\text{Cs}_2\text{Co}(\text{HSeO}_3)_4 \cdot 2\text{H}_2\text{O}$

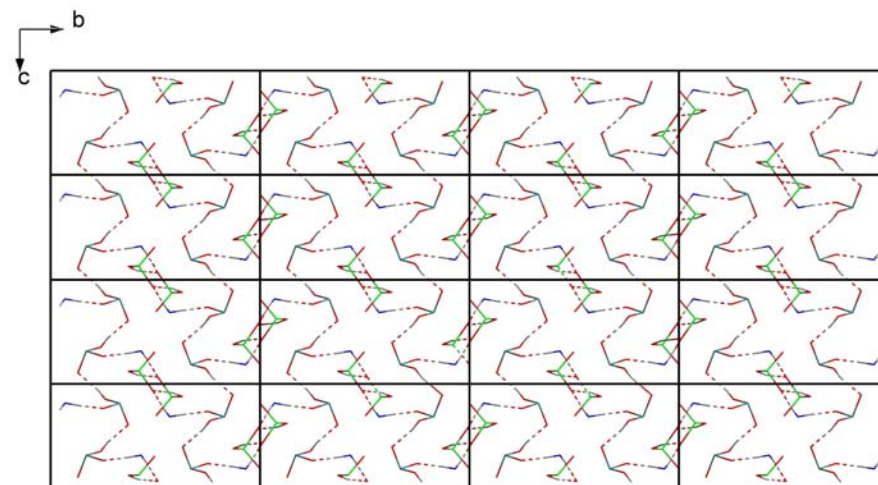


Connectivity of the coordination polyhedra of $\text{Cs}_2\text{Co}(\text{HSeO}_3)_4 \cdot 2\text{H}_2\text{O}$

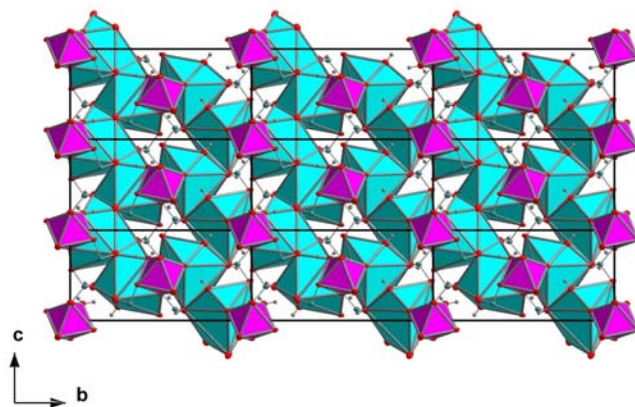
Results



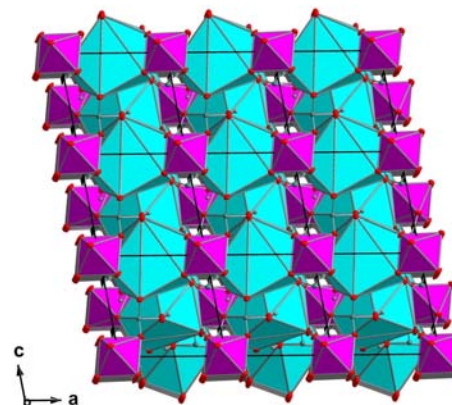
Hydrogen bonds of $\text{Cs}_2\text{Co}(\text{HSeO}_3)_4 \cdot 2\text{H}_2\text{O}$



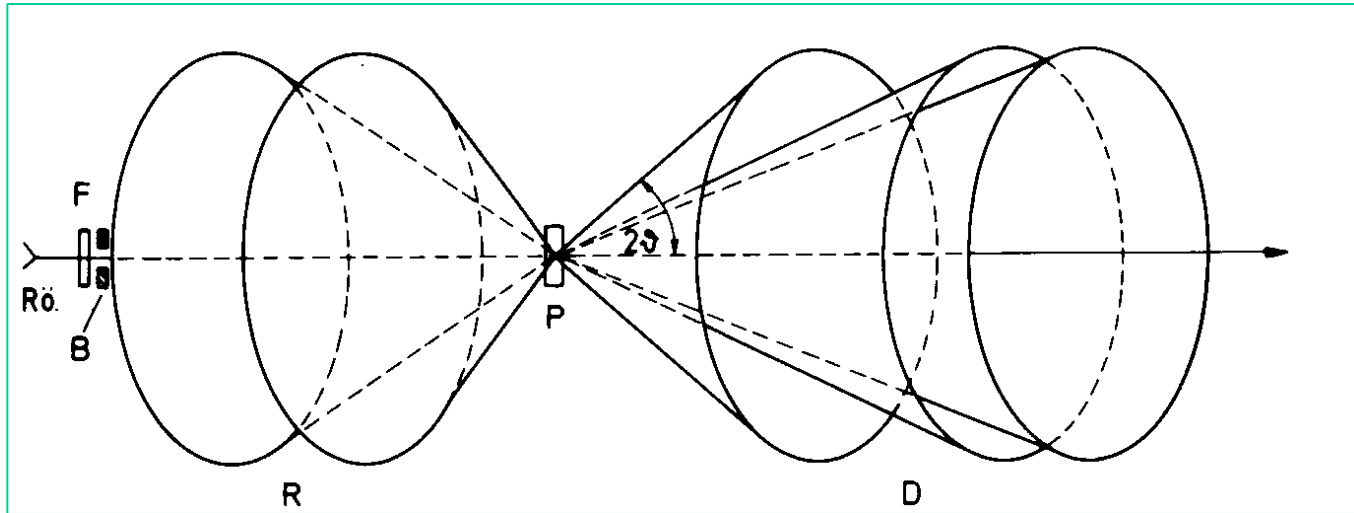
Anions and hydrogen bonds of $\text{Cs}_2\text{Co}(\text{HSeO}_3)_4 \cdot 2\text{H}_2\text{O}$



Crystal structure of $\text{Cs}_2\text{Co}(\text{HSeO}_3)_4 \cdot 2\text{H}_2\text{O}$



4.3 X-ray powder diffraction (principle)

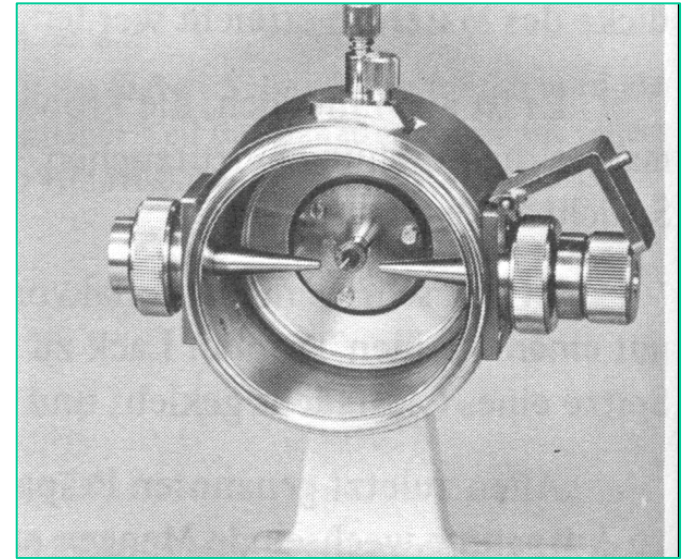
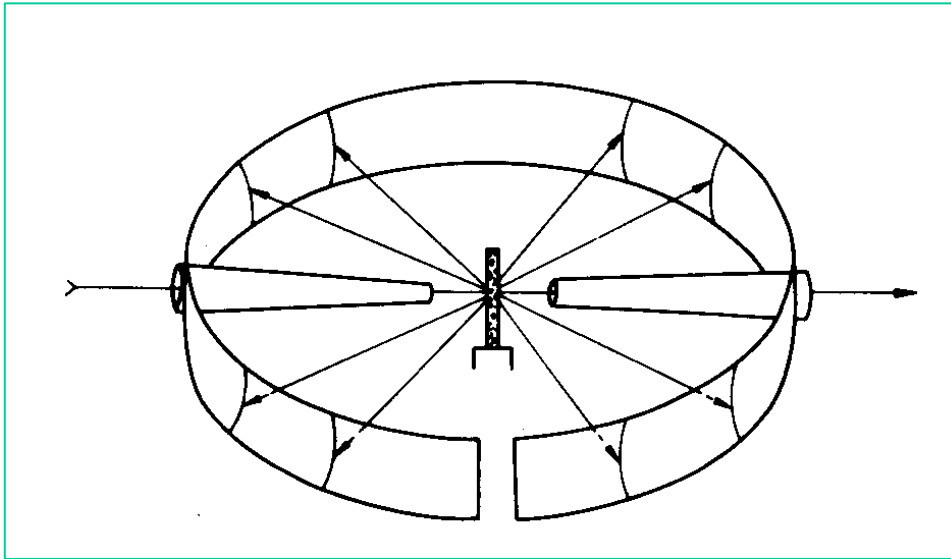


Because of the random orientation of the crystallites in a powder sample, X-ray diffraction results in cones of central angle θ_{hkl} with high intensity of scattered beams each representing a set of lattice planes hkl with the corresponding Bragg angle θ_{hkl} and spacing d_{hkl} .

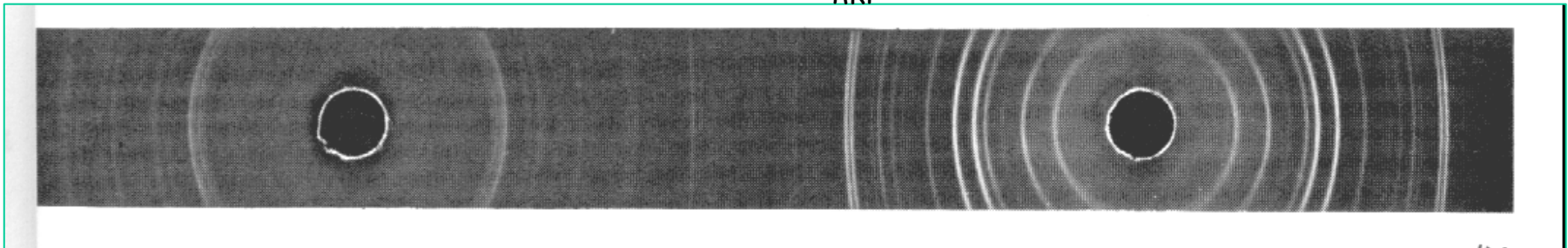
Above conditions are due to **Bragg's** law/equation.

$$\boxed{\frac{1}{d_{hkl}} = \frac{2 \cdot \sin \theta_{hkl}}{\lambda}} \quad \text{or} \quad \boxed{\lambda = 2 \cdot d_{hkl} \cdot \sin \theta_{hkl}} \quad \text{or} \quad \boxed{d_{hkl} = \frac{\lambda}{2 \cdot \sin \theta_{hkl}}}$$

4.3 X-ray powder diffraction (Debye-Scherrer Geometry)



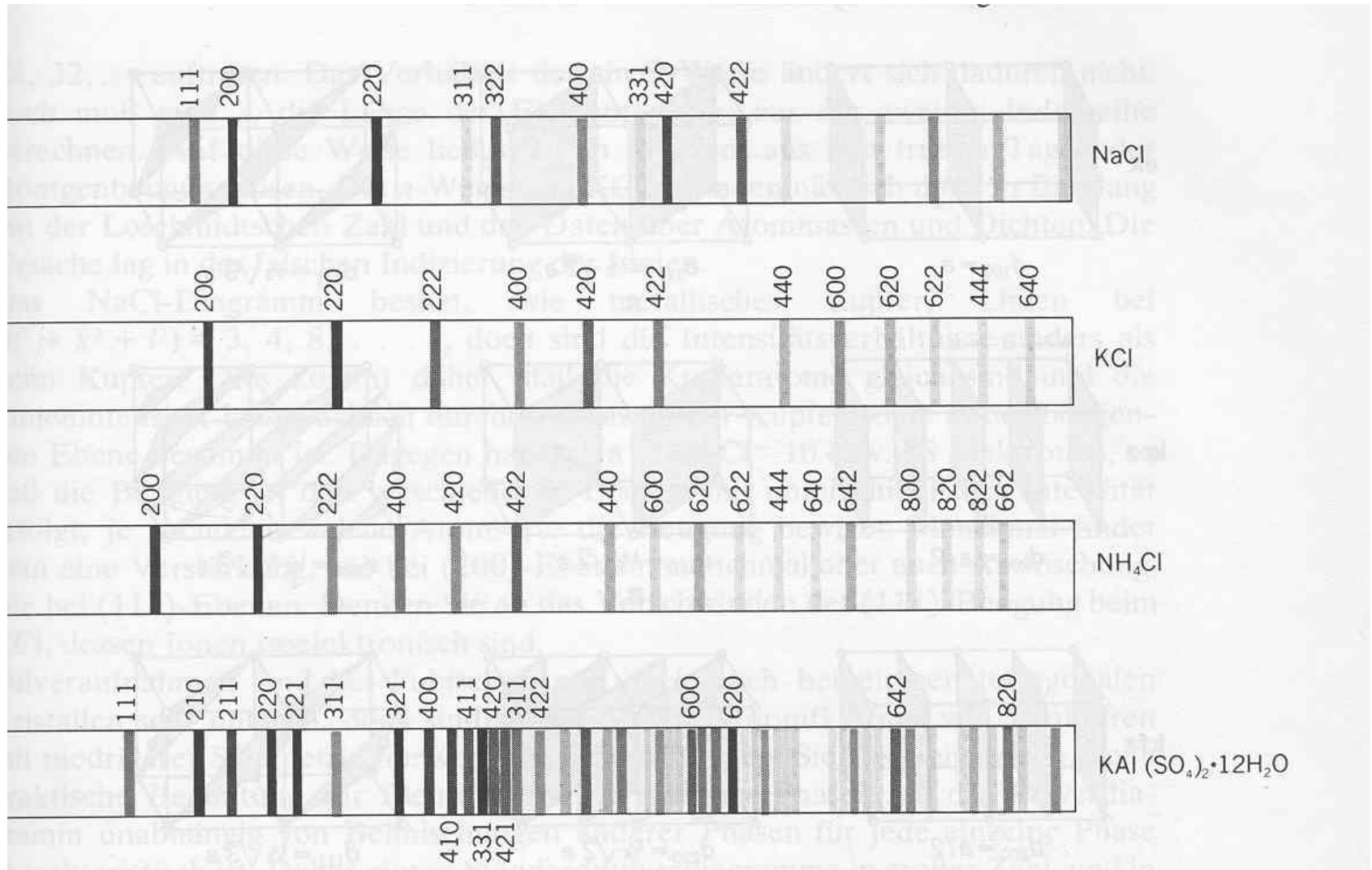
$$\leftarrow \text{-----} 180^\circ \geq 2\theta_{hkl} \geq 0^\circ \text{-----} \rightarrow$$



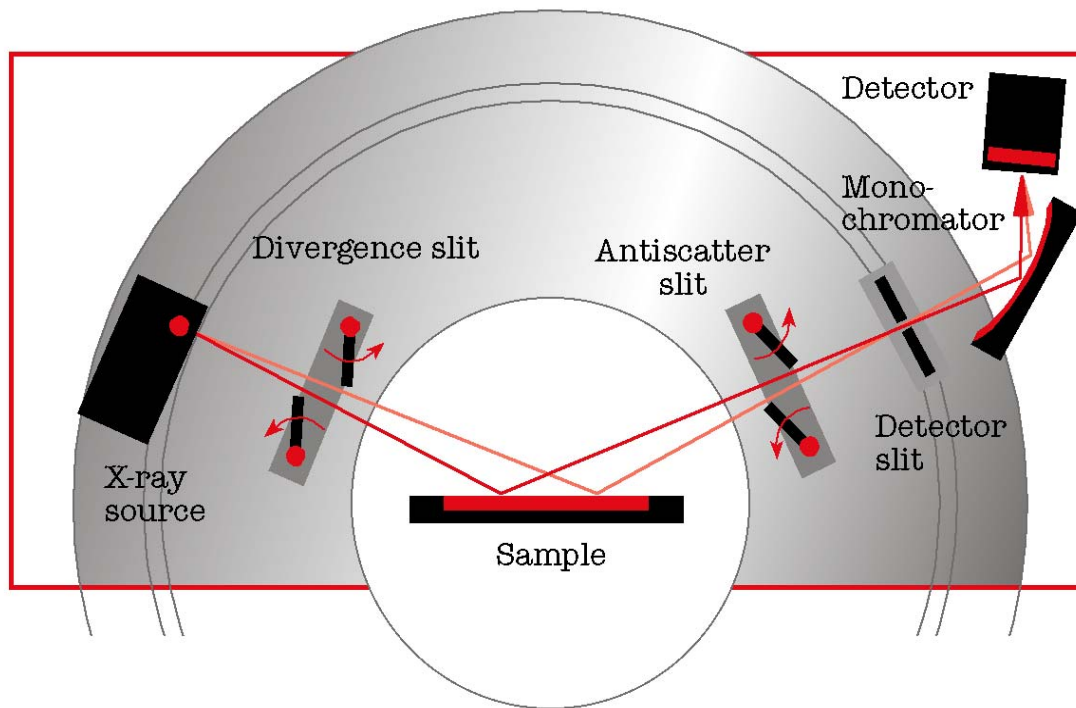
$$\leftarrow 360-4\theta_{hkl} \rightarrow$$

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

4.3 X-ray powder diagrams: Miller indices of Bragg reflections



4.3 X-ray powder diffraction (Bragg-Brentano diffractometer)



Bragg-Brentano diffractometer

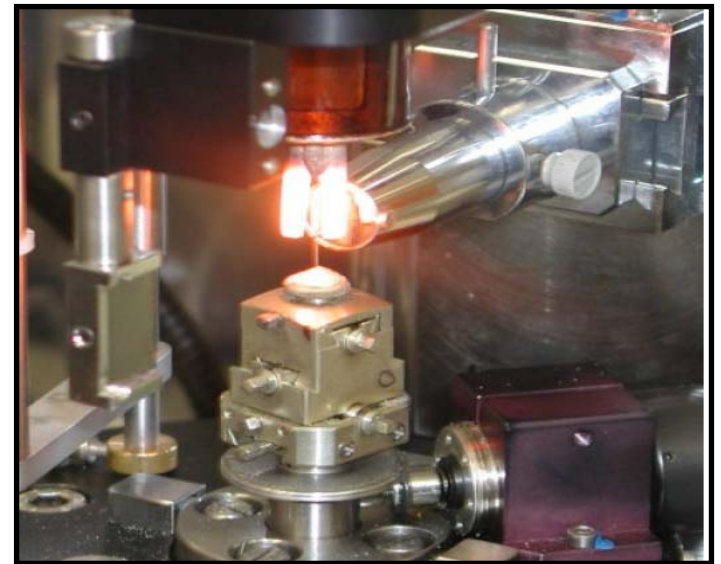
4.3 X-ray powder diffraction (polycrystalline samples)



Powder diffractometer (STOE)



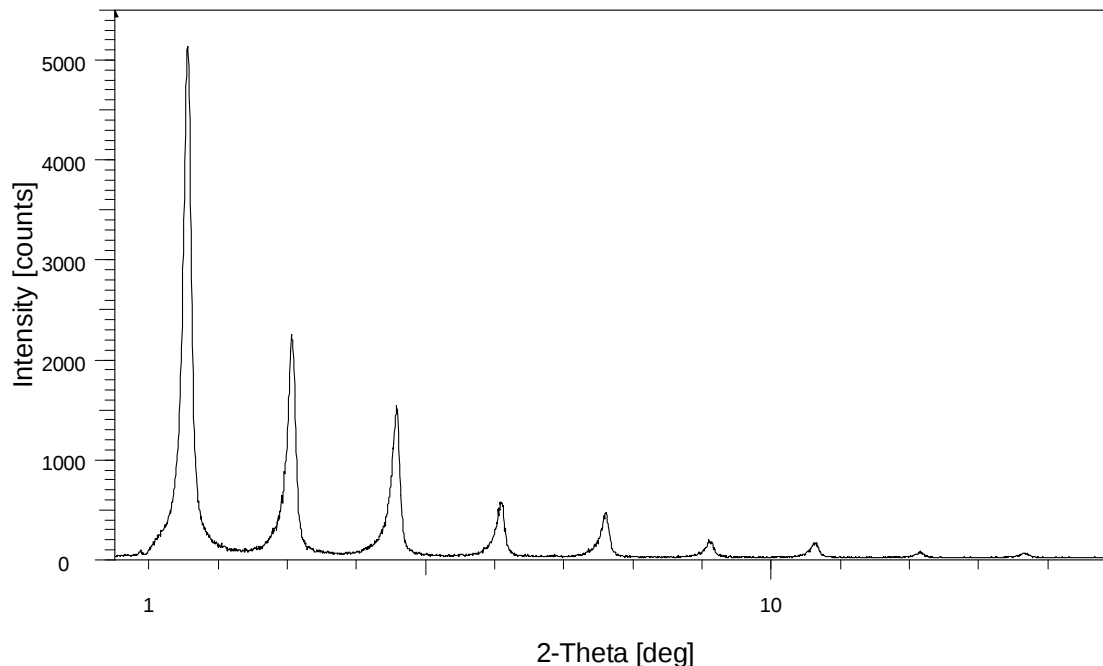
Powder
sample
holder



Goniometer head

4.3. X-ray powder diffraction (Bragg-Brentano Geometry)

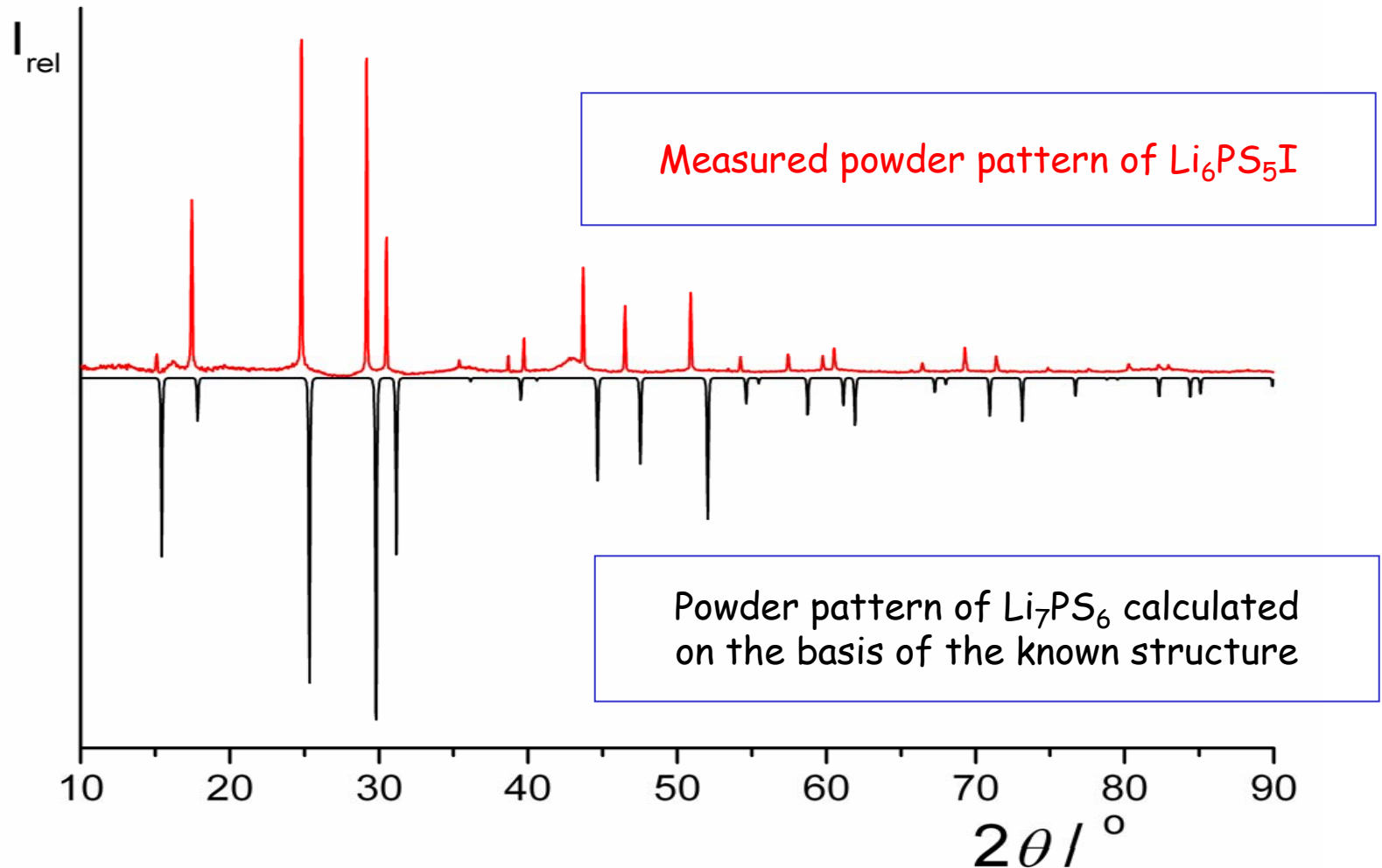
Silver-Behenate



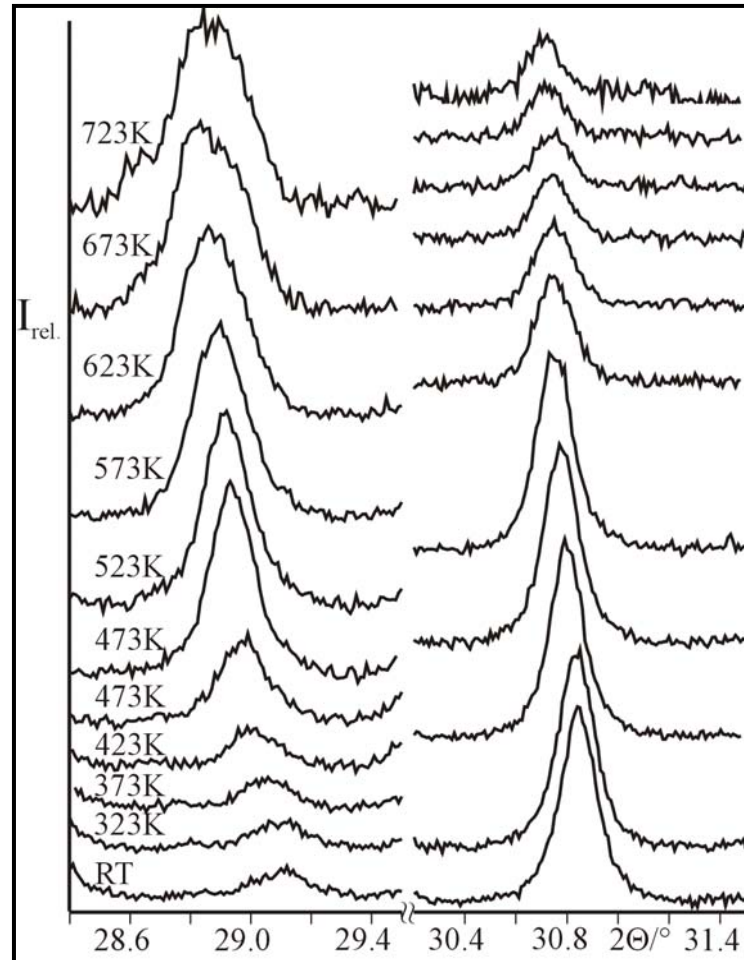
Agbehenate 0.1dg divergence 2.3 soller 1-3mm slits ni filt - Type: 2Th/Th locked - Start: 0.500 ° - End: 19.998 ° - Step: 0.007 ° -

- D8 ADVANCE,
- Cu radiation, 40kV / 40mA
- Divergence slit: 0,1°
- Step range: 0.007°
- Counting time / step: 0.1 sec
- Velocity: 4.2°/minute
- Total measure. time: 3:35 min.

4.3 X-ray powder diffraction (analysis)



4.3 X-ray powder diffraction



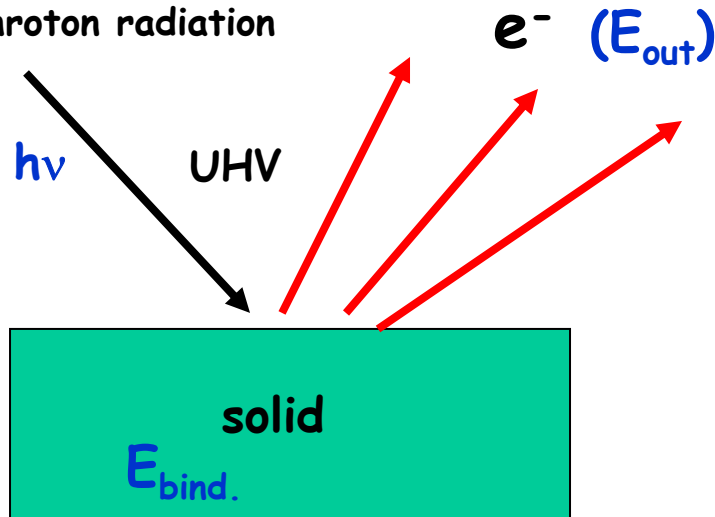
Temperature dependent X-ray powder diffraction diagram

4.4 Photoemission or Photoelectron spectroscopy: ESCA

ESCA = Electron Spectroscopy for Chemical AnalAysis

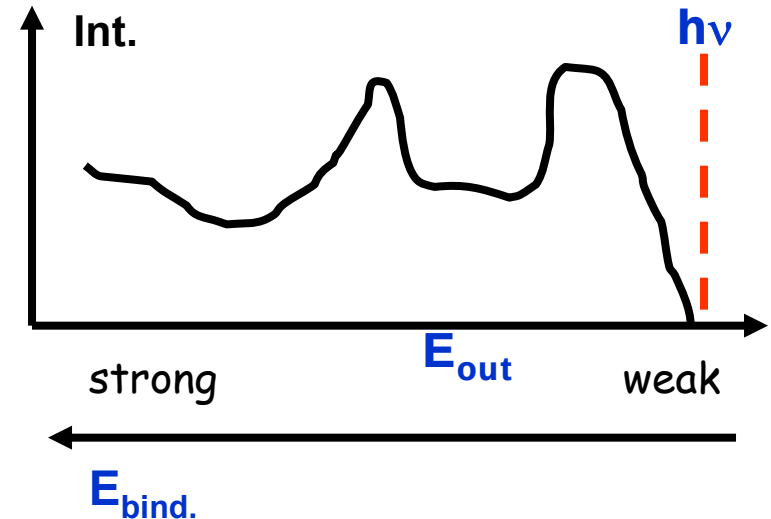
Basic equation: $E_{\text{out}} = h\nu - E_{\text{bind.}}$

UV, X-Ray or
synchrotron radiation



The spectrum of the emitted electrons is analyzed with respect to:

- energy
- momentum
- spin



- the higher the binding energy ($E_{\text{bind.}}$) the lower the E_{out} !
- ESCA is particularly a surface sensitive method (UHV !)

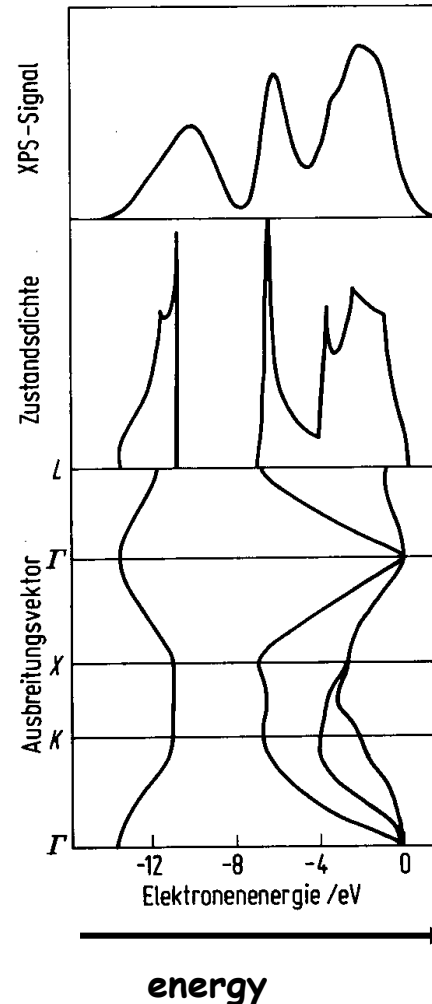
4.4 ESCA measurement for solids: band structure

UV, X-ray or
synchrotron radiation

UHV

e^-

solid



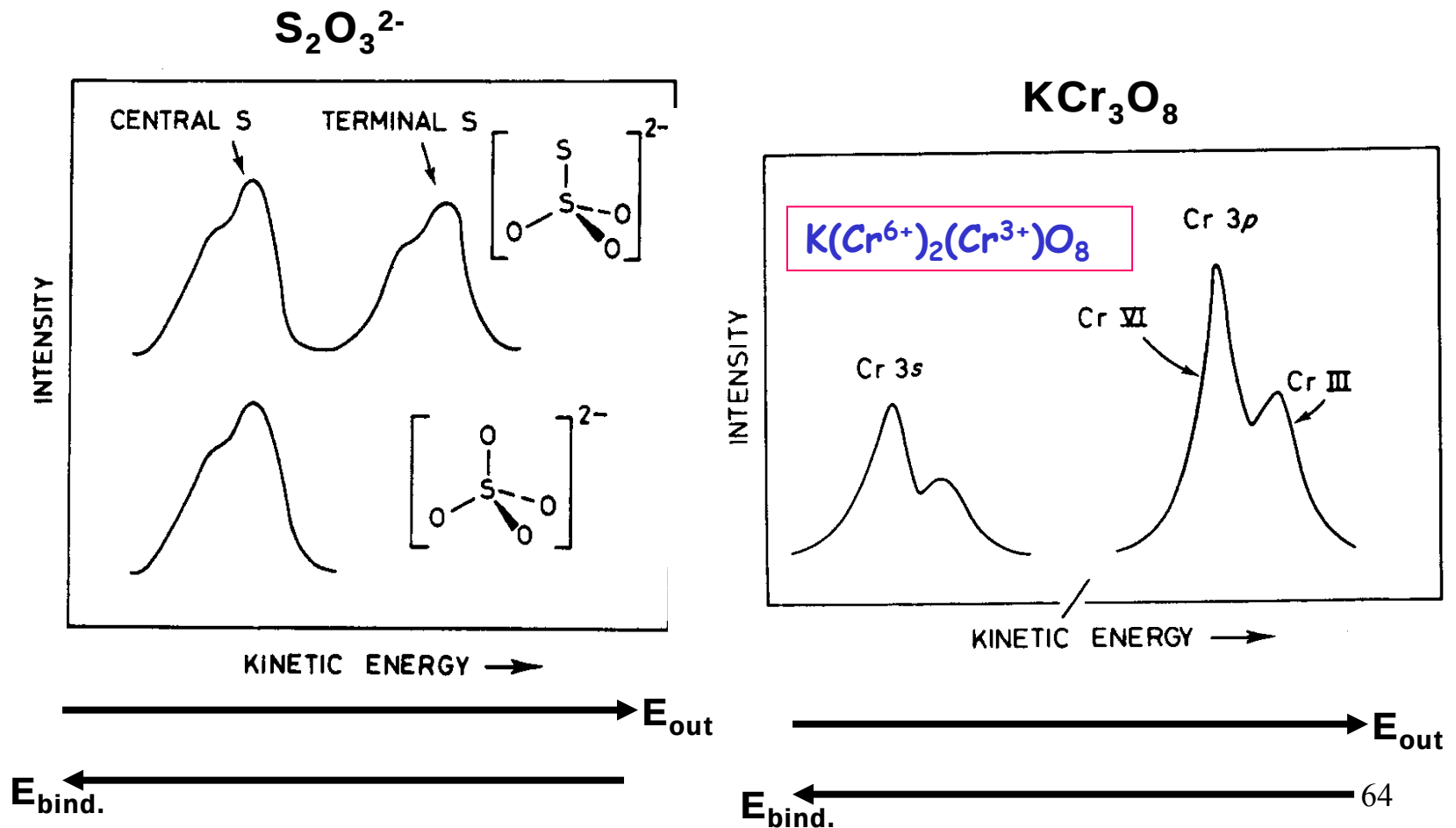
UPS spectrum

DOS
(below E_F)

Band structure
(chemical bonding in
different directions of a
crystalline solid)

4.4 Typical ESCA spectra for molecules: functionality of atoms in molecules

- Analysis of the energy levels of electrons in molecules („chemical shift“)



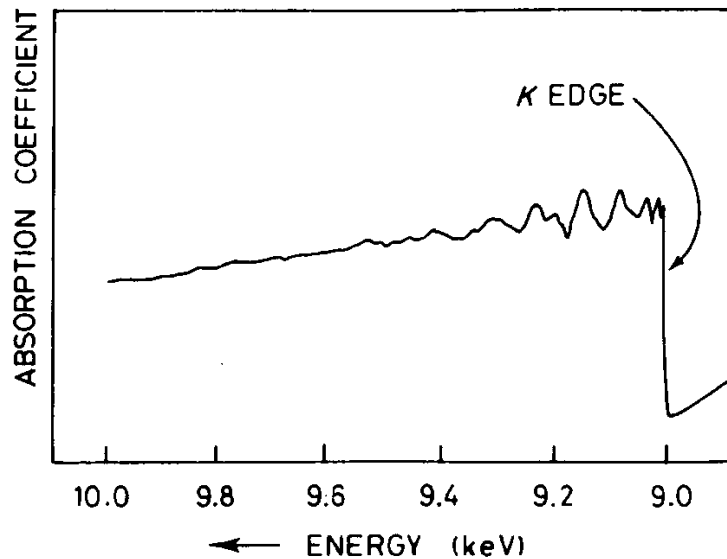
4.5 X-ray absorption spectroscopy: EXAFS, XANES

Spectroscopical methods associated with specific physical effects at/near characteristic X-ray absorption edges:

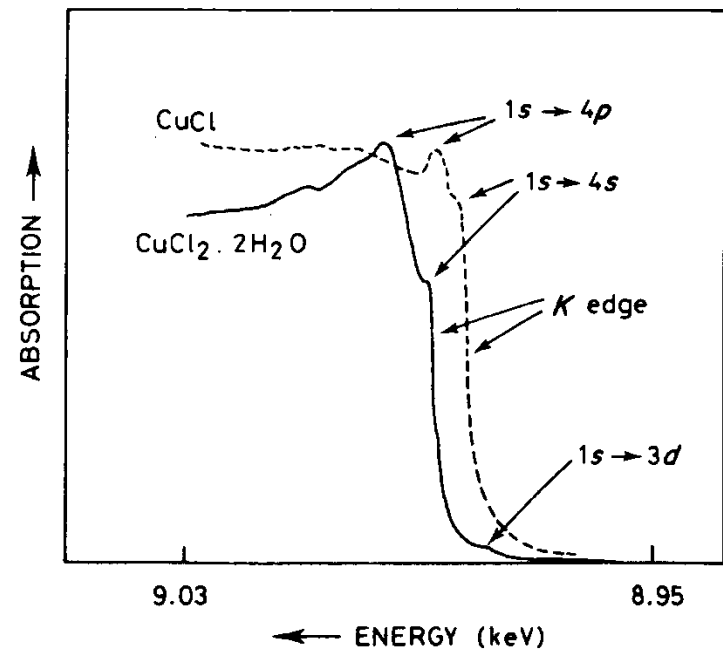
EXAFS: Extended X-Ray Absorption Fine Structure

XANES: X-Ray Absorption Near Edge Structure

- tunable synchrotron radiation in the X-Ray region necessary



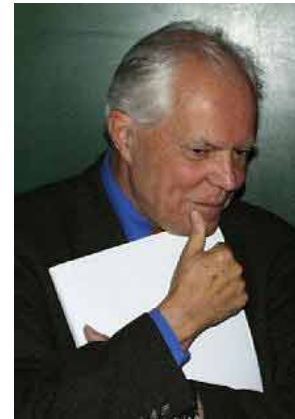
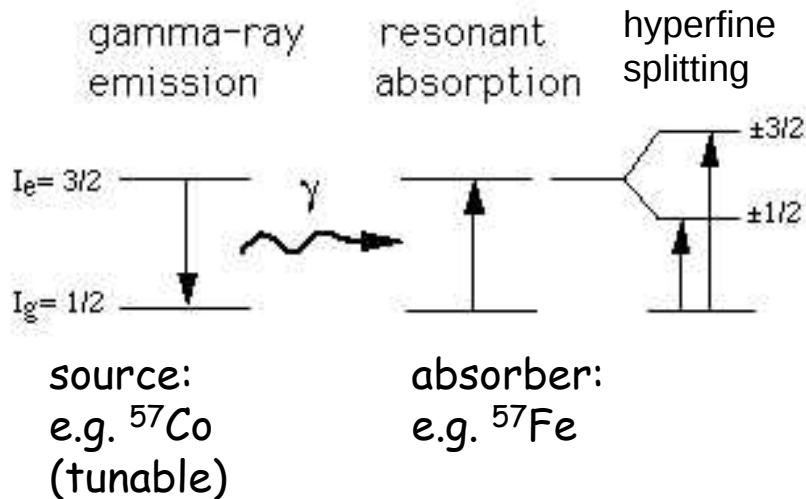
EXAFS spectrum of Cu (K edge)
(information about the coordination of Cu)



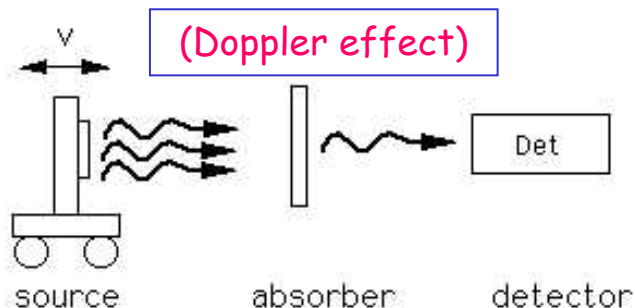
Near K edge structure of Cu in two
Cu compounds (information about the
oxidation state)

4.6 Moessbauer Spectroscopy

→ The nucleus of the specific isotope of an atom embedded in a solid (e.g. ^{57}Fe = absorber) is excited by γ -rays emitted by an unstable isotope of a neighbor element (e.g. ^{57}Co = source). Slow mechanical movement of the source modifies the emission energy (Doppler effect) and allows resonance absorption in the absorber. The resonance energy depends significantly on the chemical surrounding of the absorber atom



R. Moessbauer
N.P. 1961



frequently applied for
→ ^{57}Fe , ^{119}Sn , ^{127}J ...

→ chemical surrounding (symmetry, coordination number, oxidation state, magnetism) of atoms with these nuclei in a solid can be probed in a highly sensitive way ($\sim 10^{-8}$ eV)

4.6 Moessbauer Spectroscopy

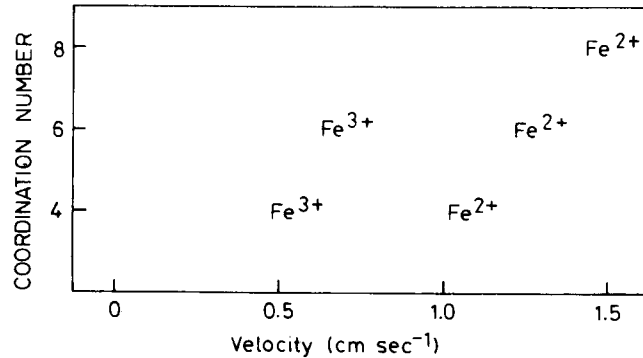


Fig. 4.27 Chemical shifts in iron-containing compounds. (From Bancroft, *Mössbauer Spectroscopy*, McGraw-Hill, 1973)

Two major informations from Moessbauer spectra:

a) „Chemical Shift“

(not to be confused with the same term in NMR and ESCA)

→ oxidation state

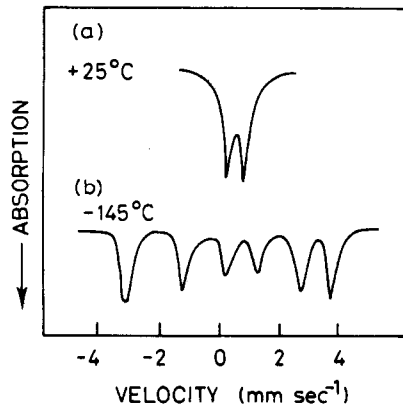


Fig. 4.28 Mössbauer spectrum of KFeS_2 (a) above and (b) below the Néel temperature. (From Greenwood, *Chem. Brit.*, 3, 56, 1967)

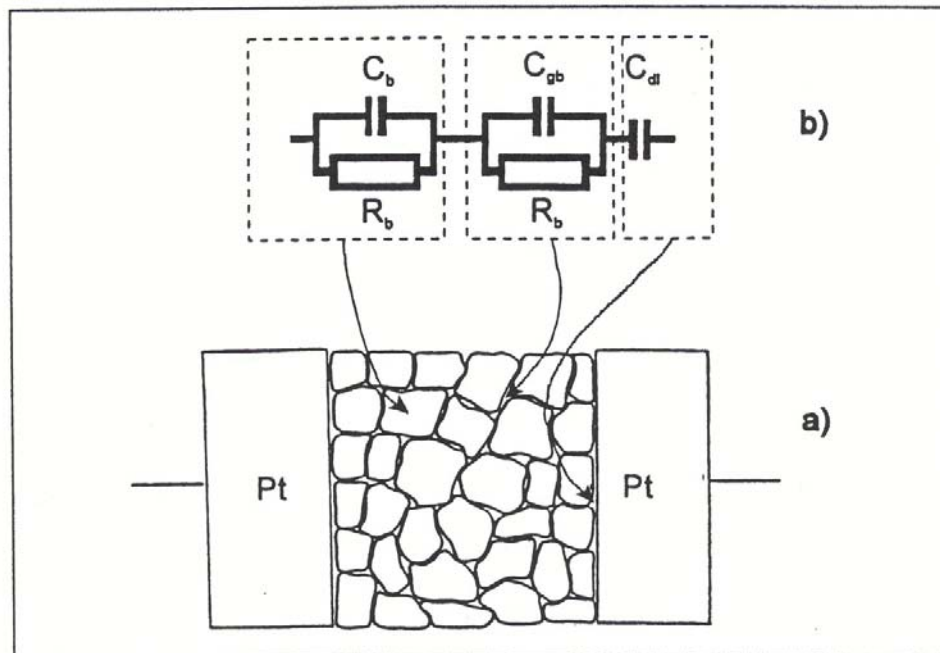
b) Hyperfine Splitting

→ magnetic interactions, symmetry

4.7 Impedance spectroscopy (basic aspects)

Purpose: Exploring the electrical behavior of a microcrystalline solid sample as a function of an alternating current (ac) with a variable frequency.

(note: differences between ac-/dc- and ionic/electronic conduction !!!)



Three basically different regions for the exchange interactions between current and sample:

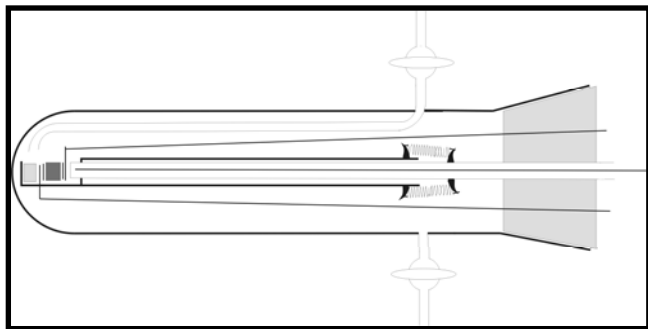
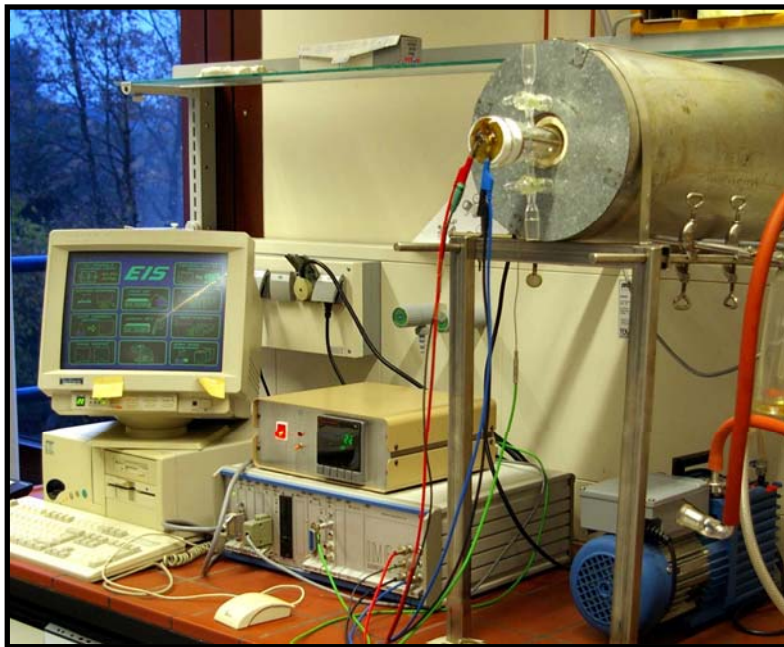
a) inside the grains („bulk“)

b) at grain boundaries

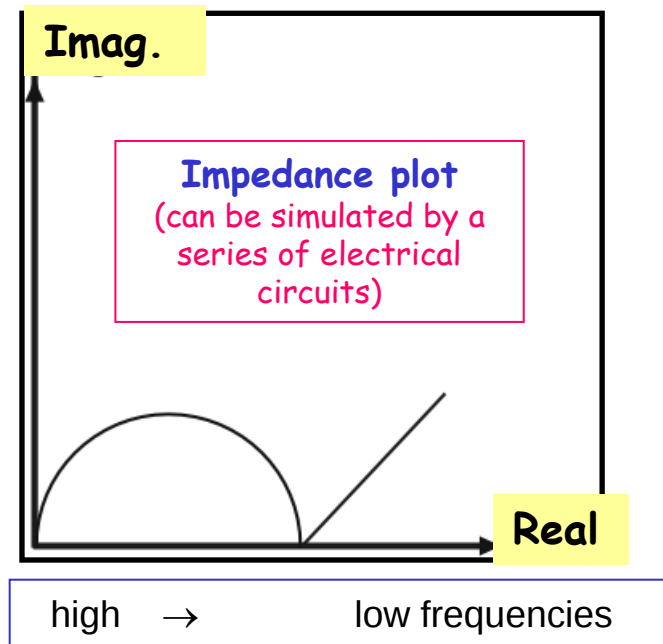
c) surface of the electrodes

The electrical behavior is simulated by a suitable combination of RC circuits: R = resistivity, C = capacity

4.7 Impedance device and impedance plot for an ionic conductor



Idealized impedance plot (Nyquist diagram) for an ionic conductor



4.7 Impedance spectroscopy: example

(after V. Nickel, H.-J. Deiseroth et al.)

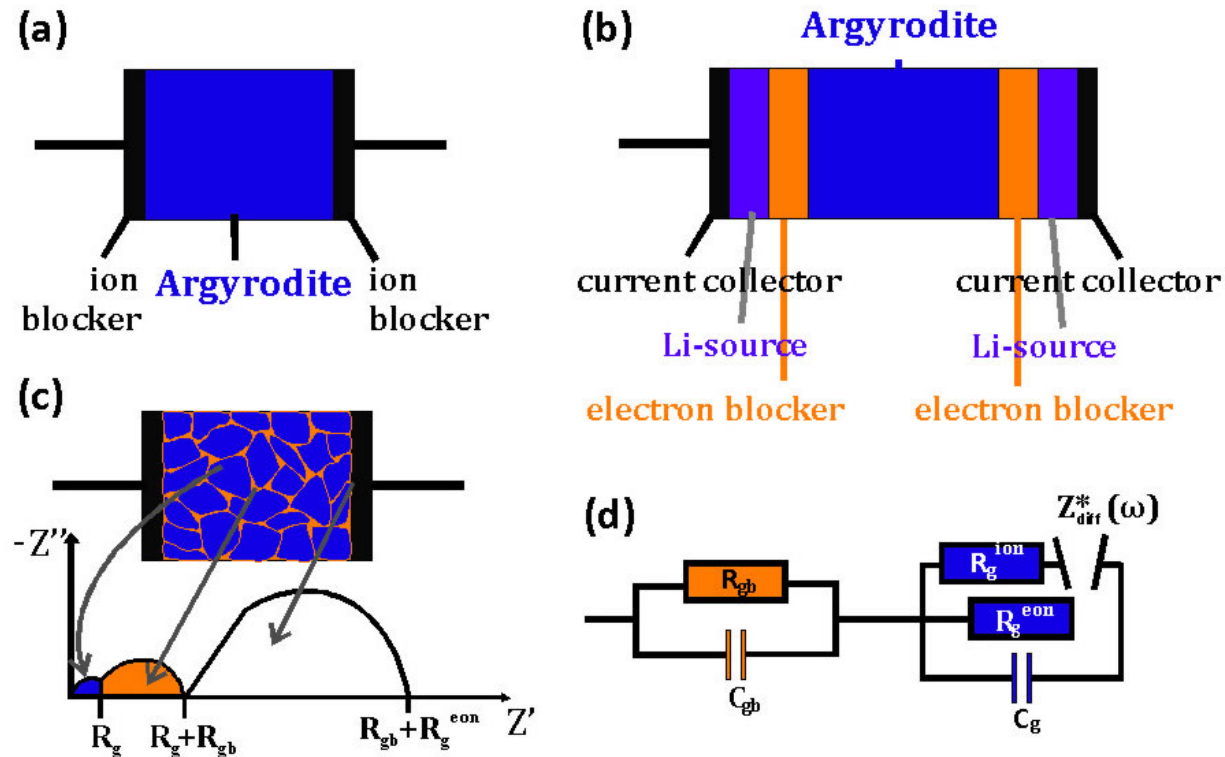


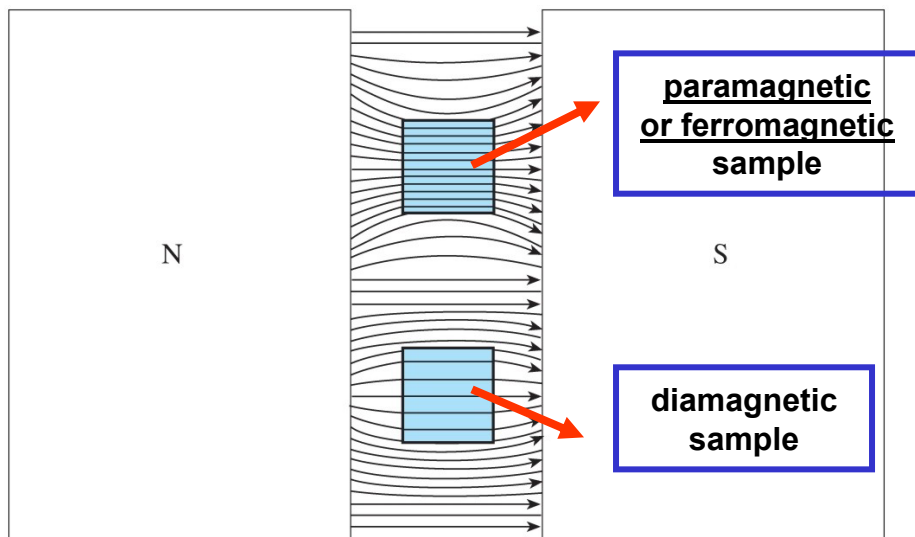
Figure 1:

(a, b) Symmetric cell for electrochemical measurements with (a) ion blocking or (b) electron blocking electrodes

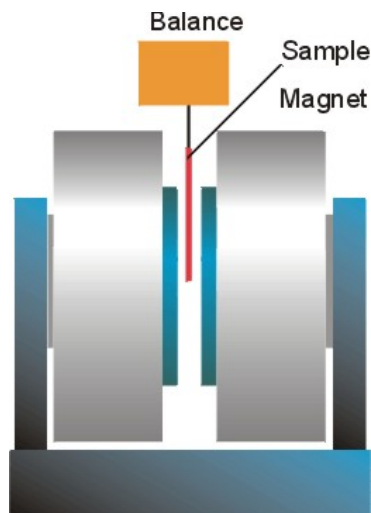
(c) Schematic representation of a cell with a polycrystalline sample pellet and selective ion blocking electrodes and the resulting impedance spectrum

(d) Respective equivalent circuit with the active impedance elements (for electron blockage, Z_{diff}^* is in series with R_g^{eon}) C_g, C_{gb} : bulk-, grain boundary capacitance; R_g, R_{gb} : bulk-, grain boundary resistance; Z_{diff}^* : diffusion impedance

4.8 Magnetic measurements: Gouy-balance and squid magnetometer



a



Gouy balance

SQUID: Superconducting Quantum Interference Device

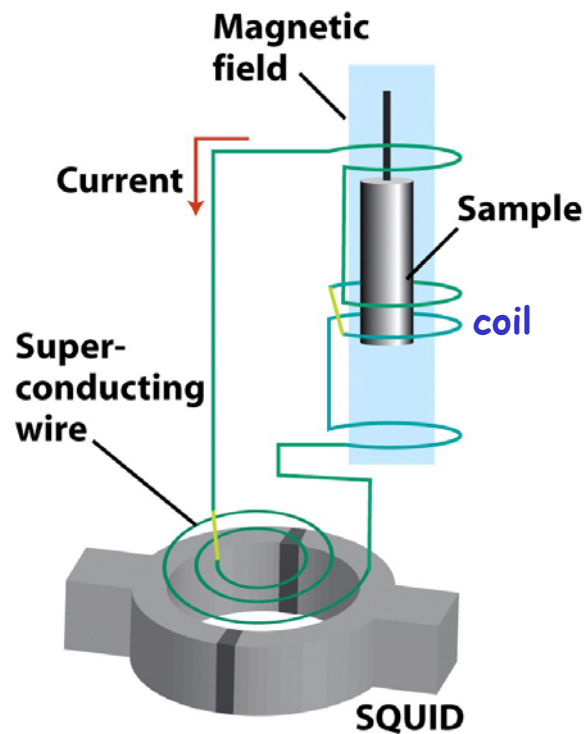


Figure 6-29
Shriver & Atkins Inorganic Chemistry, Fourth Edition
© 2006 by D. F. Shriver, P. W. Atkins, T. L. Overton, J. P. Rourke, M. T. Weller, and F. A. Armstrong

Based on the **quantization of magnetic flux** by a „weak link“ (**Josephson contact**) in a superconducting wire (loop) that allows the tunneling of „**Cooper pairs**“.

4.9 Thermal Analysis: DTA (Differential Thermal Aalysis)

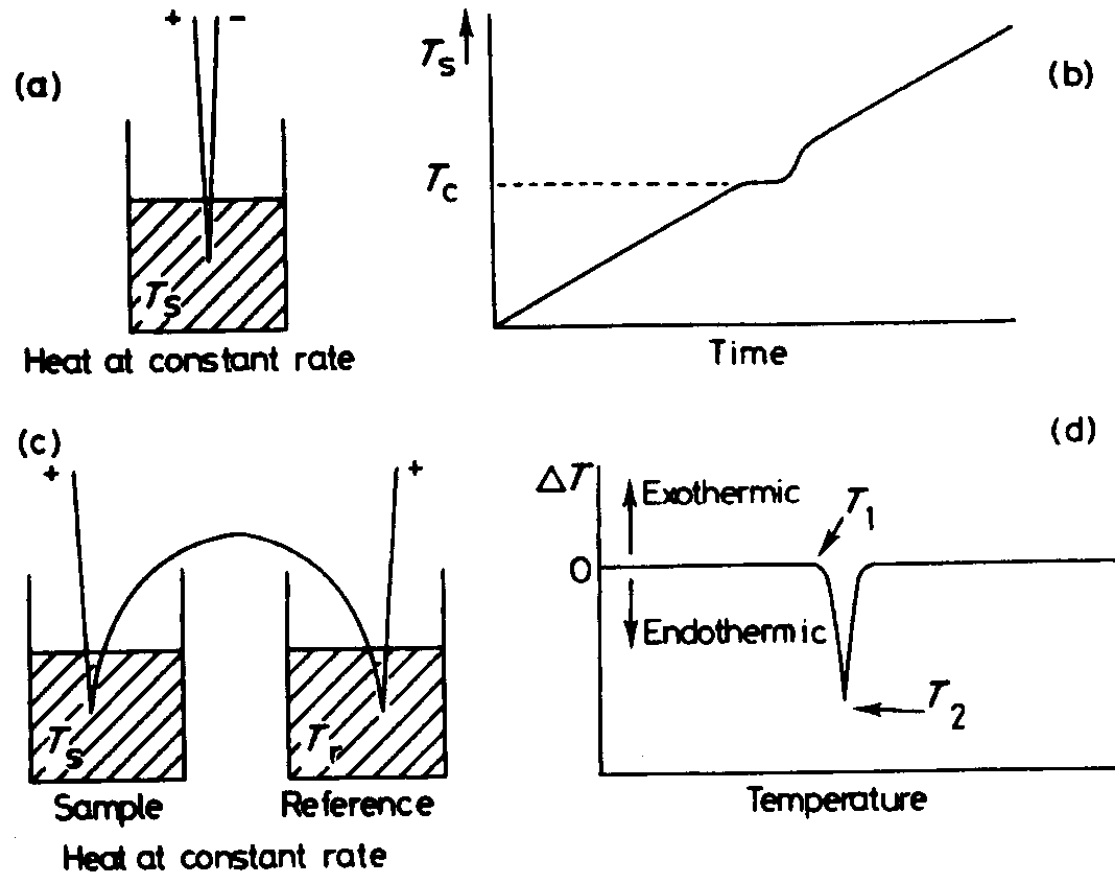
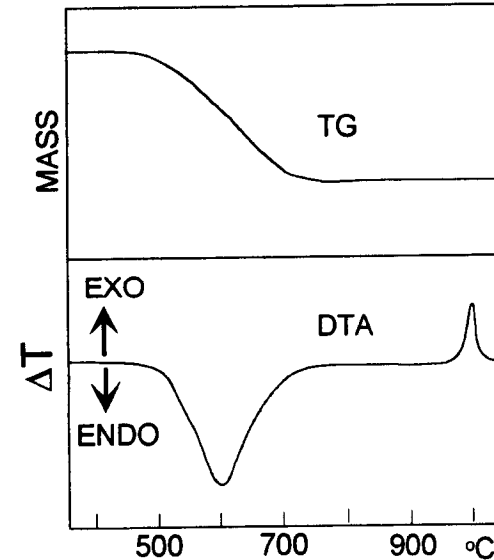
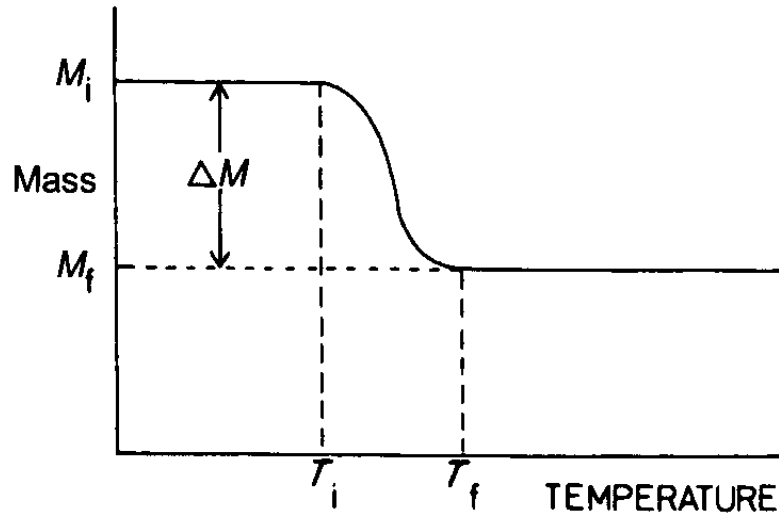


Fig. 4.31 The DTA method. Graph (b) results from the set-up shown in (a) and graph (d), a typical DTA trace, results from the arrangement shown in (c)

4.9 Thermal analysis: TG (Thermogravimetry)

(Mass change during heating or cooling, combinable with DTA)



Other variants of thermal analysis

:

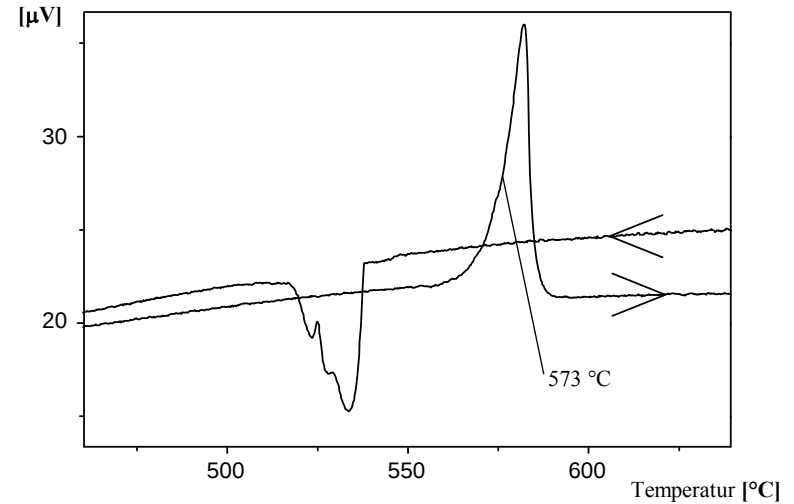
DSC: Differential Scanning Calorimetry

- Quantitative measurement of enthalpy changes

TMA: Thermo Mechanical Analysⁱs (e.g. dilatometry)

- Mechanical changes that occur upon temperature changes

4.9 Thermal analysis: DSC (Differential Scanning Calorimetry) (-170 °C to 700°C)



4.10 Comparison of some techniques for structural studies

Comparison of some physical techniques for structural studies

Technique	Nature of the Effect	Information	Interaction time	Sensitivity	Comments
X-ray diffraction	Scattering, mainly by electrons, followed by interference ($\lambda = 0.01\text{--}1\text{ nm}$)	Electron density map of crystal	10^{-18} s but averaged over vibrational motion	crystal $ca. 10^{-3}\text{ cm}^3$	Location of light atoms or distinction between atoms of similar scattering factor difficult in presence of heavy atoms
Neutron diffraction	Scattering, mainly by nuclei, followed by interference ($\lambda = 0.1\text{ nm}$)	Vector internuclear distances	10^{-18} s but averaged over vibrational motion	crystal $ca. 1\text{ cm}^3$	Extensively used to locate hydrogen atoms. May give additional information due to spin $\frac{1}{2}$ on neutron leading to magnetic scattering
Electron diffraction	Diffraction (atom or molecule) mainly by nuclei, but also by electrons ($\lambda = 0.01\text{--}0.1\text{ nm}$)	Scalar distances due to random orientation	10^{-18} s but averaged over vibrational motion	100 Pa (1 Torr)	Thermal motions cause blurring of distances. Preferably only one (small) species present. Heavy atoms easy to detect
Microwave	Absorption of radiation due to dipole change during rotation ($\lambda = 0.1\text{--}30\text{ cm}$; 300–1 GHz in frequency)	Mean value of r^{-2} terms; potential function	10^{-10} s	10^{-2} Pa (10^{-4} Torr)	Mean value of r^{-2} does not occur at r_e even for harmonic motion. Dipole moment necessary. Only one component may be detected. Analysis difficult for large molecules of low symmetry
Vibrational infrared	Absorption of radiation due to dipole change during vibration ($\lambda = 10^{-1}\text{--}10^{-4}\text{ cm}$)	Qualitative for large molecules	10^{-13} s	100 Pa (1 Torr)	Useful for characterization. Some structural information from number of bands, position and possibly isotope effects. All states of matter

4.10 Comparison of some techniques for structural studies

Comparison of some physical techniques for structural studies

Technique	Nature of the Effect	Information	Interaction time	Sensitivity	Comments
Vibrational Raman	Scattering of radiation with changed frequency due to polarizability change during a vibration ($\lambda = \text{visible usually}$)	Qualitative for large molecules	10^{-14} s	10^4 Pa (100 Torr) (ν^4 dependent)	Useful for characterization. Some structural information from number of bands, position, depolarization ratios, and possibly isotope effects. All states of matter
Electronic	Absorption of radiation due to dipole change during an electronic transition ($\lambda = 10\text{--}10^2$ nm)	Qualitative for large molecules	10^{-15} s	1 Pa (10^{-2} Torr)	Useful for characterization. Some structural information from number of bands and position. All states of matter
Nuclear magnetic resonance	Interaction of radiation with a nuclear transition in a magnetic field ($\lambda = 10^2\text{--}10^7$ cm; 3 KHz to 300 MHz)	Number of magnetically equivalent nuclei in each environment	$10^{-1}\text{--}10^{-9}$ s	10^3 Pa (10 Torr (^1H))	Applicable to solutions and gases. In conjunction with molecular weight measurements may be possible to choose one from several possible models
Mass spectrometry	Detection of fragments by charge/mass	Mass number, plus fragmentation patterns	—	10^{-9} Pa (10^{-11} Torr)	Useful for characterization of species in a vapour, complicated by reactions in spectrometer. Does not differentiate isomers directly. Important for detecting hydrogen in a molecule

From I. R. Beattie, *Chem. Soc. Rev.*, **4**, 107 (1975). Used with permission.

4.10 Comparison of some techniques for structural studies

Information sought	Phase of sample		
	Gas	Liquid or solution	Solid
Fingerprint ^a	IR * <i>Microwave</i> Mass spec. UV/vis * <i>UPS</i>	IR, R NMR Mass spec. ^b UV/vis	IR, R Powder X-ray diffraction Mass spec. ^b UV/vis
Groups present	IR Mass spec. NMR	IR, R Mass spec. ^b NMR	IR, R Mass spec. ^b *NMR * <i>Mössbauer</i>
Molecular symmetry	IR ^c * <i>Microwave</i> **ED	IR, R NMR	IR, R *NMR ** <i>NQR</i> Single crystal X-ray diffraction
Bond lengths and angles	IR, R ^d * <i>Microwave</i> **ED	*** <i>EXAFS</i> LCMNR	Single crystal X-ray diffraction ***Neutron diffraction
Electronic structure ^e	UV/vis *UPS ESR	UV/vis ESR * <i>XPS</i>	UV/vis *UPS *XPS * <i>Mössbauer</i> ** <i>NQR</i> Single crystal X-ray and neutron diffraction